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MODELLING, MATHEMATICAL ANALYSIS, NUMERICAL SOLUTION AND PARAMETER IDENTIFICATION IN REACTION SYSTEMS

Noemí Esteban Rodríguez

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[Modelling, mathematical analysis, numerical solution and parameter identification in reaction systems.]

D. Alfredo Bermúdez de Castro López-Varela
Dña. Oana Teodora Chis

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A mis padres,
Emilio y Rosa

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Preface

In general terms, a chemical reactor can be understood as a vessel used in transforming the initial chemical species into desired final products. They can be ideal reactors, for example, stirred tank reactors (STR) in the simplest cases, or more complex reactors such as fixed bed reactors (FBR). In any case, it is important that the residence time inside the reactor be sufficiently large to produce the expected chemical reactions.

The design of the reactors involves three main fields in chemical engineering: thermodynamics, kinetics and heat transfer. Thus, when a reaction occurs in a batch STR reactor, a reasonable question would be "What is the maximum expected conversion?". This is a question related to thermodynamics. If we want to know how long the reaction should take to convert the reactants in the desired products, we would be asking ourselves about the kinetics (we should know both the stoichiometry and the reaction rates). Finally, if we want to know how much heat must be transferred to the reactor or from it to keep the isothermal condition, we are dealing with a heat transfer problem combined with thermodynamics (we must know if the reaction is endothermic or exothermic).

In order to describe more in detail a reactor it is necessary to distinguish among different types. In the literature there are many reactor classifications. Each one is performed according to the feature to be highlighted. Now, we describe the main classifications following the scheme from [29].

Operation types: This classification is related to the operational configuration of the reactor. This is the classification we use *a priori* in the present thesis (batch STR, semi-batch, CSTR, PFR or FBR are different reactors according to their operational configuration).

1. *Batch stirred tank reactor (Batch STR)*: reactants are introduced into the reactor at the initial time only. There are no input or output flows along the process.

2. *Semi-batch Batch (Semi-batch STR)*: some of the reactants are introduced in the reactor at the initial time; some others are continuously introduced along the process.
3. *Continuous (flow) stirred tank reactor (CSTR)*: reactants are continuously introduced along the time. There is also an output flow along the process.
4. *Plug flow reactors (PFR)*: the plug flow is a tubular reactor in which the so called plug flow assumption is considered. That is, the velocity is constant on any cross-section of the pipe.
5. *Fixed bed reactors (FBR)*: the fixed bed reactor is a single cylindrical shell with convex heads with a packed bed of catalytic particles of uniform size, which are immobilized or fixed within the tube.

Number of phases: Reactors can also be classified by the number of phases present in the reactor at any time. They are called *homogeneous* and *heterogeneous* reactors. The first ones represent the reactors with only one phase (STRs are homogeneous reactors). The second ones contain more than one phase. Several heterogeneous reactor types are available due to various combinations of phases (like PFRs or FBRs).

Reaction types: This classification is made considering different type of reactions. Some of the most important are:

1. *Catalytic:* reactions that require the presence of a catalyst to obtain the necessary rate conditions. An example of these reactors is the FBR.
2. *Noncatalytic:* reactions that do not include either a homogeneous or heterogeneous catalyst. They are the opposite to the previous ones.
3. *Autocatalytic:* in this reaction scheme one of the products increases the rate of reactions.
4. *Biological*: reactions that involve living cells (enzymes, bacteria, etc.).
5. *Polymerization:* reactions that involve formation of molecular polymer chains.

Finally, depending on the final destination in industry we consider a classification in concordance with two different motivations:

1. *Industrial reactors*: simulation of its operation with the ultimate aim of optimizing it economically by modifying the operating conditions (initial conditions, temperature, ...).

2. *Laboratory reactors/pilot plant*: optimization of the reactor design: optimal geometric and optimal operating conditions for a future reactor. The goal of the design is to determine the reactor features such as pipe, valves or mixers. For example, the reactor must have sufficient volume to allow the reaction reach a level of conversion or allow the heat exchange necessary.

Reactor design requires first to establish the type and size of the reactor and then the operation type according to the chemical process, as explained in [24]. Important considerations are related to the chemical reactions and, in any of the described reactors, reaction velocity expressions (kinetics) must be known. The reaction rate involves a mathematical expression. In order to predict the size of the reactor needed to obtain both the desired conversion of reactants and a fixed output of the product, it is required information on the composition and temperature changes, as well as reaction rate, obtained from the mole and energy balance equations.

Assuming available experimental data and known stoichiometry (the reactions), we must search for an identification methodology for determining the best kinetic model. There are several techniques available in the literature, such as differential, integral and incremental methods [12]. The **differential method** compares the right-hand side of the model with the derivatives of the data. The **incremental method** works with the "extent" concept, which provides an analytic solution of a new decoupled system. The **integral method** solves numerically the model and compares it with the data. In any case, an optimization problem is constructed, depending on the kinetic parameters. Furthermore, if better results are desired, a combination of these methods is recommended.

In a theoretical framework, the mathematical analysis of the models mentioned above has driven out curiosity in the spirit of scientific inquiry. Particularly, the general convection-diffusion-reaction equations have enjoyed a considerable amount of scientific interest. They can be studied from different approaches using a variety of different methods from many areas of mathematics. Some of those studies are based on bifurcation and stability or semigroup theory, or variational approach. After the theoretical analysis a natural question is related to the numerical solution of the model. It can be based on finite difference schemes, in most of the cases, and in a few others on finite elements method.

This thesis is divided in three different parts in which an extensive study of reactors is done, from theoretical and practical point of view. It is complemented with three appendices describing some tools and results used throughout the thesis in order to get a self-contained work. In the following we describe

briefly the contents of each part.

I Modelling chemical reactors

The first part is devoted to the description of the reactors we are interested in. At first, we recall basic concepts about chemical species and reactions. We also introduce the functional form of reaction velocities recalling the most important ones from the literature ([46], [34] and [31]). They play an important role in Part III. Next, we formulate the models of the main STR reactors (batch, semi-batch and CSTR), with mole and energy balance equations, both in transient and steady state, and assuming constant density. These models are extensively used in industry, specifically in kinetic identification [17]. Then, we describe the general convection-diffusion-reaction model that will be applied in the analysis of a particular reactor of this type, namely PFR. The existence and uniqueness of solution is studied and the behaviour of the error is analyzed when numerical methods are employed. Finally, we obtain the FBR model, describing the boundary conditions and distinguish between two cases, resistance and not resistance. This reactor is the most complex of those considered in this work. In fact, its mathematical analysis is beyond the scope of this thesis.

II Mathematical analysis and numerical solution

In this part an extensive study is done for the convection-diffusion-reaction model beginning with the mathematical analysis for the $n-$dimensional reactor and then numerical solution of the reactor models is designed. The proof of local existence and uniqueness of solution is based on the semigroup theory. The global existence is proved via L^∞ estimates exploding two properties (called **(P)** and **(M)**) described in Chapter 4. In Chapter 5 an error estimation is obtained following the techniques from [63]. *A priori* we have proved the existence of solution of the semi-discretized problem, using the Picard-Lindelöf theorem. For the numerical solution we use a finite difference scheme for the PFR model and a finite element method for the FBR model.

III Identification in reaction systems

This last part is related to model identification. More precisely, it deals with the identification of the best kinetic model from a list of proposed functional forms, and also of the values of its corresponding parameters by means of an optimization process. In order to solve the problem, we use a combination of an incremental and an integral method. The idea of the first one is to decompose the identification task into a set of subproblems, one for each kinetic model. Meanwhile, the second one is based on a direct comparison of species measurements and computed concentrations

via the theoretical model. Due to this, the second method is obviously more expensive and works better with the parameters obtained from the incremental method. Such identification processes are usually studied in systems where the phenomena of interest can be observed in isolation, without other physical phenomena. This is the case for the identification of reaction kinetics in liquid phase, where a stirred batch or semi-batch reactor is used in the majority of cases, as explained in [17]. For this reason, we focus on stirred tank reactors, using a set of experimental data and the reactions taking place. A catalogue of kinetic models containing the parameters to be identified will be provided too.

Appendices

Appendix A summarizes the general equations of continuum thermomechanics for reacting mixtures.

Appendix B describes some basic definitions and theorems of semigroup theory needed in the proof of local existence theorem.

Appendix C describes some useful bounds for the error estimates.

Appendix D contains a summary of this dissertation in Spanish.

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Part I

Modelling chemical reactors

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Introduction

Chemical reactors are widely used by chemical engineers in industry to transform raw materials into final products. The main purposes are related to maximizing benefits, which is equivalent to "design" an optimal reactor, and thus minimizing the production costs. Hence, adequate modelling and correct analysis are essentials. Together with chemical kinetics they are the scientific basis for the analysis of most engineering procedures, occurring in nature or related to synthetic processes.

An important part in reactor modelling is the reaction rate that represents the measure of the variation in concentration of the reactants or the variation in concentration of the products per unit time. Reaction rate can be *a priori* understood, independently of the reactor shape and length. The overall chemical process also depends on the reactor size.

Many processes have been traditionally modelled as ideal reactors: stirred tank or plug flow reactors. This type of modelling is mainly based on the reactor features and phenomena such as heat or mass transfer.

In the first chapters we formulate the mathematical modelling of stirred tank reactors (STR) and plug flow reactors (PFR). We consider both the transient and the steady-state cases. Reactors are not supposed to be either adiabatic or isotherm, so temperature as well as species concentrations have to be computed by the models that are obtained from the energy and mass conservation equations, respectively.

Firstly, we consider lumped parameter models (or zero-dimensional models), where the thermo-mechanical magnitudes do not depend on the particular position in the reactor. They correspond to the so-called stirred tank reactors. We write mathematical models for batch and semi-batch STR and also for continuous STR. Then we describe plug-flow reactors (PFR). In this case, the thermo-mechanical magnitudes depend on a spatial variable (as well as on time). Hence, the mathematical models are described by partial differential equations involving derivatives with respect to spatial variable and time.

The mathematical model for a reaction-diffusion system was initially derived from the work of Alan Turing in 1952 [65] and it was used for the first time in

chemistry. However, it can also describe dynamical processes of non-chemical nature. Some fields of application are biology, geology, physics, epidemiology, oncology or environmental engineering processes, among others.

From a qualitative point of view, a reaction-diffusion system is a mathematical model describing how the concentration of one or more substances varies over time and space under the influence of two terms: the reaction term, in which concentrations are generated or degenerated by interaction, and diffusion that generates substances expansion in space.

The idea of Chapter 2 in this modelling part is to consider the model described in Chapter 1 as a general $n-$dimensional model which can be particularized to recover the PFR model. The mathematical model is a coupled system of partial differential equations involving gradient and laplacian with respect to spatial variables and partial time derivative.

Finally, the most sophisticated reactors we consider are the fixed bed reactors (FBR). As explained in [57], the first commercial application of these reactors dates from 1831 when a vinegar maker developed a process for making sulfur trioxide using air and sulfur dioxide in bed of platinum sponge previously heated. After that, he patented it. Since the catalyst was not consumed, the continuous flow of reactants was passed over the bed, without the need of recycling the catalyst. Nowadays, the typical application is related to the design and development of a catalyst that improves the conversion of an intermediate product to the final product.

These reactors are understood in this thesis as heterogeneous reaction systems in which plug-flow is assumed. The model is based on the conservation laws for mass, energy and momentum and lead to partial differential equations. We consider a multi-scale model. The bed is modelled as a continuum of small particles (solids) containing the catalyst and interacting with the fluid. This particles are consider of spherical shape and hence spherical symmetry is assumed. The fluid bulk is modelled as a fluid flowing in a porous media. We have be to careful with the coupling between the models.

Chapter 1

Modelling stirred tank reactors

The study of reactors is initially performed by means of ideal models. Stirred tank reactors are a good example of these kind of reactors, as a perfectly mixed volume is considered and the behaviour of the reacting system is not influenced by the fluid dynamic conditions.

In this chapter we introduce models for both transient and steady-state stirred tank reactors (STR). We focus on the three following stirred tank reactors types:

- *Batch STR*: reactants are introduced into the reactor at initial time only. There are no input/output flows along the process.

- *Semi-batch STR*: some of the reactants are introduced in the reactor at the initial time; some others are continuously introduced along the process.

- *Continuous (flow) stirred tank reactor (CSTR)*: reactants are continuously introduced along the time. There is also an output flow along the process.

The main assumption in these reactors is that the mixture inside is perfectly homogeneous because of stirring, so the physico-chemical magnitudes do not depend on position.

1.1 Modelling chemical reactions

In this section we introduce the tools needed to construct the reaction term in the model. Let us consider a set of reacting chemical species:

$$\mathcal{S} = \{E_1, \ldots, E_N\}.$$

Let $\mathcal{M}_i$ be the molecular mass of species E_i. All species are involved in a set of L chemical reactions

$$\nu_1^l E_1 + ... + \nu_N^l E_N \to \lambda_1^l E_1 + ... + \lambda_N^l E_N, \qquad 1 \le l \le L,$$

where ν_i^l and λ_i^l, $i = 1, \ldots, N$, $l = 1, \cdots, L$ are called ***stoichiometric coefficients***.

1.1.1 Chemical species and elements. Conservation relations

Let us suppose that the species are formed by K different chemical elements, named H_k, $1 \le k \le K$. Let the formula of species E_i be

$$E_i = (H_1)_{h_{1i}} \cdots (H_K)_{h_{Ki}}, \quad 1 \le i \le N. \tag{1.1}$$

Since atoms are conserved in chemical reactions, we have

$$\sum_{i=1}^{N} h_{ki}\nu_i^l = \sum_{i=1}^{N} h_{ki}\lambda_i^l, \quad k = 1, \cdots, K,\ l = 1, \cdots, L.$$

Matrix $(H)_{ki} = h_{ki}$ is called ***element (or atomic) matrix***. The above relations can be written in a more compact form as follows

$$HA = 0,$$

where A is the stoichiometric matrix:

$$(A)_{il} := \lambda_i^l - \nu_i^l, \quad i = 1, \cdots, N,\ l = 1, \cdots, L.$$

From the mass conservation in the l-th chemical reaction

$$\sum_{i=1}^{N} \mathcal{M}_i\lambda_i^l = \sum_{i=1}^{N} \mathcal{M}_i\nu_i^l, \quad l = 1, \cdots, L$$

we can easily deduce that

$$A^t\boldsymbol{\mathcal{M}} = \mathbf{0}, \tag{1.2}$$

where $\boldsymbol{\mathcal{M}}$ is the column vector of the molecular masses of species.

Hence,

$$\dim(\ker(A^t)) \ge 1.$$

1.1.2 Finite rate chemical reactions

For elementary reactions, the law of mass action (C.M. Guldberg and P. Waage in [44]) yields the following expression for the velocity of the l-th reaction:

$$\hat{\delta}_l(\theta, y_1, \ldots, y_N) = \hat{k}_l(\theta) \prod_{j=1}^{N} y_j^{\nu_j^l}. \tag{1.3}$$

Along this work we will focus on these reaction rate functional forms and assume that coefficients ν_j^l are positive integer numbers.

Many other reactions can be modelled by similar functions, but with exponents that are different from the stoichiometric coefficients on the left-hand side of the reaction, namely,

$$\hat{\delta}_l(\theta, y_1, \ldots, y_N) = \hat{k}_l(\theta) \prod_{j=1}^{N} y_j^{\alpha_j^l}. \tag{1.4}$$

In general, δ_l can be any function. Examples of kinetics different from the mass action law are the Hill [34] or Michaelis-Menten kinetics [46].

1.1.3 Reaction rate constant

Factor $k_l = \hat{k}_l(\theta)$ is called ***reaction rate constant*** of the l-th reaction. As the notation indicates, it is not constant but a function of the reactor temperature θ through the

Arrhenius law

$$\hat{k}_l(\theta) = B_l exp\Big(\frac{-E_{a_l}}{\mathcal{R}\theta}\Big), \tag{1.5}$$

where B_l is the pre-exponential factor, E_{a_l} is the activation energy of the l-th reaction and $\mathcal{R}$ is the universal gas constant.

1.2 Modelling Batch Stirred Tank Reactors

The batch reactors are typically used in industry in many processes such as dissolution of solids, mixing reactants, chemical reactions, polymerization, among others.

These reactors consist of a container with a mixer. Their dimensions can vary in a large range from less than 1 litre to more than 10000 litres. They are usually built with steel, glass-lined steel or glass. Reactants are usually introduced at the top of the reactor at the beginning of the process. We can see the illustration of the reactor below:

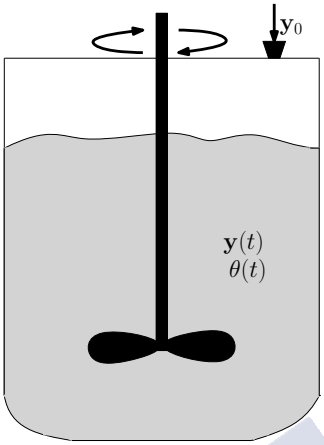

Figure 1.1: Batch Stirred Tank Reactor

We consider the case where the mixture density can be assumed to be constant. In order to derive the full model, we need to compute the composition, temperature and density of the reacting mixture along time, so several ODEs must be introduced.

The species conservation equations

In transient Batch STRs time evolution of concentrations y_i $(kmol/m^3)$, of the chemical species E_i, $i = 1, \ldots, N$, satisfy the following system of ODEs:

$$\frac{d(Vy_i)}{dt} = V \sum_{l=1}^{L} (\lambda_i^l - \nu_i^l) \hat{\delta}_l(\theta, y_1, \ldots, y_N),$$

where function δ_l is the velocity of the l-th reaction and $V(t)$ (m^3) is the volume occupied by the mixture at time t.

In order to get a well-posed problem, initial conditions must be prescribed; more precisely, the initial concentration of each species $y_{0,i}$ must be given. Finally, the model can be written in matrix form as follows:

$$\frac{d(V\mathbf{y})}{dt} = VA\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}), \tag{1.6}$$

$$\mathbf{y}(0) = \mathbf{y}_0. \tag{1.7}$$

The energy equation

Sometimes the temperature is given. This is the case, for instance, if the reactor is isothermal. Otherwise, the temperature evolution must be computed by a model that arises from the energy conservation principle.

Let us assume that the reactor exchanges heat with its surroundings. We denote by $\theta_{ext}(t)$ the outside temperature along time and by $g(t)$ (W/K) the heat transfer coefficient between the reactor and its surroundings. If $e(t)$ (J/kg) denotes the specific internal energy of the mixture and $\rho(t)$ its density at time t, then the total internal energy is given by $V(t)\rho(t)e(t)$ and the energy conservation principle yields the ordinary differential equation

$$\frac{d(V\rho e)}{dt} = g(\theta_{ext} - \theta). \tag{1.8}$$

We want to eliminate e from this equation in terms of θ. Let us assume that for each species there is a function $\hat{e}_i(\theta)$ giving internal energy from temperature (this is usually true for liquids and also for perfect gases):

$$e_i(t) = \hat{e}_i(\theta(t)),$$

with

$$\hat{e}_i(\theta) := e_i^* + \int_{\theta^*}^{\theta} \hat{c}_i(s)\, ds,$$

where e_i^* is the internal energy of formation of the i-th species at the reference temperature θ^* (usually, θ^* is taken to be the so-called standard temperature, i.e., 25^oC) and $c_i = \hat{c}_i(\theta)$ is the specific heat of the i-th species $(J/(kgK))$. For the mixture,

$$e(t) = \sum_{i=1}^{N} Y_i(t) e_i(t),$$

where $Y_i(t)$ denotes the mass fraction of species E_i at time t which is related to the concentration by

$$Y_i = \frac{\mathcal{M}_i y_i}{\rho}.$$

Hence,

$$\rho e = \sum_{i=1}^{N} \rho Y_i e_i = \sum_{i=1}^{N} \mathcal{M}_i y_i e_i$$

and then

$$\frac{d(V\rho e)}{dt} = \sum_{i=1}^{N} \mathcal{M}_i \Big(\frac{d(Vy_i)}{dt} e_i + V y_i \frac{de_i}{dt}\Big) = V \sum_{i=1}^{N} \mathcal{M}_i \Big(e_i\big(A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y})\big)_i + y_i \hat{c}_i(\theta) \frac{d\theta}{dt}\Big). \tag{1.9}$$

Let us define the specific heat of the mixture c by

$$c := \sum_{i=1}^{N} Y_i c_i.$$

Then,

$$\rho c = \sum_{i=1}^{N} \mathcal{M}_i y_i c_i = \sum_{i=1}^{N} \hat{w}_i'(\theta) y_i = \hat{\mathbf{w}}'(\theta) \cdot \mathbf{y}, \tag{1.10}$$

where the components of vector $\hat{\mathbf{w}}(\theta) \in \mathbb{R}^N$ are the molar internal energies defined by

$$\hat{w}_i(\theta) := \mathcal{M}_i \hat{e}_i(\theta) \quad (J/mol).$$

By using (1.9) and (1.10), the energy equation (1.8) becomes

$$\begin{aligned} \rho c \frac{d\theta}{dt} &= -\hat{\mathbf{w}}(\theta) \cdot A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) + \frac{g}{V}(\theta_{ext} - \theta) \\ &= -A^t \hat{\mathbf{w}}(\theta) \cdot \hat{\boldsymbol{\delta}}(\mathbf{y}, \theta) + \frac{g}{V}(\theta_{ext} - \theta) \\ &= -\Delta\hat{\mathbf{H}}(\theta) \cdot \hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) + \frac{g}{V}(\theta_{ext} - \theta), \end{aligned} \tag{1.11}$$

where the components of the L-dimensional vector

$$\Delta\hat{\mathbf{H}}(\theta) := A^t \hat{\mathbf{w}}(\theta) \quad (J/mol)$$

are the ***molar heats of reaction*** at temperature θ. Hence,

$$\Delta\hat{H}_l(\theta) = \sum_{i=1}^{N} (\lambda_i^l - \nu_i^l) \mathcal{M}_i \hat{e}_i(\theta).$$

From the computational point of view, it is convenient to divide equation (1.11) by ρc,

$$\frac{d\theta}{dt} = -\frac{1}{\rho c}\Big(\Delta\hat{\mathbf{H}}(\theta) \cdot \hat{\boldsymbol{\delta}}(\mathbf{y}, \theta) - \frac{g}{V}(\theta_{ext} - \theta)\Big).$$

By using (1.10) we finally get

$$\frac{d\theta}{dt} = -\frac{\Delta\hat{\mathbf{H}}(\theta) \cdot \hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) - \frac{g}{V}(\theta_{ext} - \theta)}{\hat{\mathbf{w}}'(\theta) \cdot \mathbf{y}}. \tag{1.12}$$

Moreover, an initial condition is needed:

$$\theta(0) = \theta_0. \tag{1.13}$$

1.2.1 The transient batch STR model

Let us assume that the volume occupied by the mixture is constant along time and given (for instance, equal to the reactor volume). Then the density of the mixture is also constant and the mathematical model for the **batch STR** becomes the following initial-value problem:

$$\begin{aligned}
\frac{d\mathbf{y}}{dt} &= A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}), \\
\frac{d\theta}{dt} &= -\frac{\Delta\hat{\mathbf{H}}(\theta)\cdot\hat{\boldsymbol{\delta}}(\theta,\mathbf{y}) - \dfrac{g}{V}(\theta_{ext}-\theta)}{\hat{\mathbf{w}}'(\theta)\cdot\mathbf{y}}, \\
\mathbf{y}(0) &= \mathbf{y}_0, \\
\theta(0) &= \theta_0.
\end{aligned}$$

Remark 1.2.1. *Since the total mass of the mixture is conserved in a Batch STR, if the volume does not change, then the mixture density is also constant along time. In the case of a mixture of perfect gases, the pressure in the reactor changes along time and is given by*

$$p(t) = \rho R(t)\theta(t),$$

where $R(t)$ is the gas constant of the mixture at time t which is given by

$$R(t) = \frac{\mathcal{R}}{\mathcal{M}(t)},$$

being $\mathcal{R}$ the universal gas constant and $\mathcal{M}(t)$ is the molar mass of the mixture at time t defined by

$$\frac{1}{\mathcal{M}(t)} = \sum_{i=1}^{N} \frac{Y_i(t)}{\mathcal{M}_i}.$$

1.2.2 Steady-state Batch STR

Usually, when the outside temperature θ_{ext} is time independent from a certain time onwards, the solution of the batch STR model above tends to a steady-state solution (i.e., time independent) as the time increases. This solution is a triple $(\mathbf{y}, \theta, V)$, being $\mathbf{y}$ a vector in $\mathbb{R}^N$ and θ and V real numbers.

In the constant density case V is given. Then, the model for a steady-state batch STR is the numerical non-linear system,

$$A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) = \mathbf{0},$$

$$\Delta\hat{\mathbf{H}}(\theta) \cdot \hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) - \frac{g}{V}(\theta_{ext} - \theta) = \mathbf{0}.$$

We notice that the fact that the above systems have the same number of equations as unknowns does not imply that they have a unique solution.

1.3 Modelling Semi-Batch and Continuous Stirred Tank Reactors

Continuous stirred tank reactors, also called ***ideal stirred tank reactors*** or ***CSTR*** are, maybe, the most used reactors in chemical industry. In most cases they operate at steady state and are considered as homogeneous reactors due to their well mixing properties.

These reactors have also vessel form, but there exist a continuous input flow and, in the case of CSTR, there is also a continuous output flow. For the sake of completeness, let us assume that the input flow is obtained by mixing several streams, each of them characterized by the following magnitudes that can be function of time:

- Flow rate (m^3/s)
- Composition (in terms of concentrations, mol/m^3)
- Temperature (K)

Usually, for semi-batch STR there are only input streams, so the volume of the mixture must change along the time. In the case of CSTR there is also an output stream, so this volume could be constant.

Let P be the number of input streams. The above magnitudes are denoted by

$$\begin{aligned} u^1(t), \cdots, u^P(t) \quad & (m^3/s), \\ \mathbf{W}^1(t), \cdots, \mathbf{W}^P(t) \in \mathbb{R}^N \quad & (mol/m^3), \\ \theta^1(t), \cdots, \theta^P(t) \quad & (K). \end{aligned}$$

Regarding the outflow, we assume there is only one stream. Its composition and temperature at time t are those of the mixture in the reactor at that time. We are interested in considering the case where the output flow rate can be different from the sum of the input flow rates. Therefore, the volume of the

mixture in the reactor may change along time. In fact, the volume can also change due to changes in composition and/or temperature as in batch STR.

Let us show the images of both semi-batch and CSTR in order to illustrate the above description:

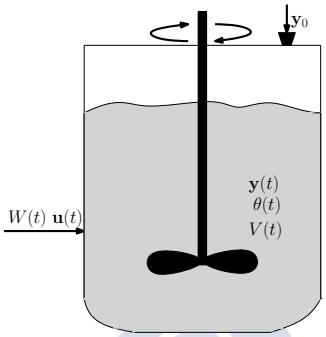

Figure 1.2: Semi-batch STR

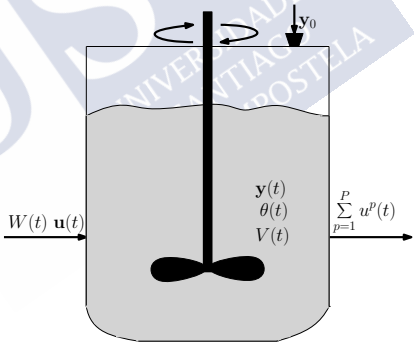

Figure 1.3: CSTR

1.3.1 The transient semi-batch and CSTR model

Firstly, the mass conservation equation (1.6) has to be replaced by

$$\frac{d(V\mathbf{y})}{dt} = VA\hat{\boldsymbol{\delta}}(t,\theta,\mathbf{y}) + W\mathbf{u} - \mathbf{y}u_{out}, \tag{1.14}$$

where $W(t)$ denotes the matrix whose columns are the vectors $\mathbf{W}^1(t), \cdots, \mathbf{W}^P(t)$. We notice that the output flow rate u_{out} is null for semi-batch STR.

Let us also notice that $\big(W(t)\mathbf{u}(t)\big)_i$ is the number of moles per second of species i entering the reactor at time t, so it is a molar flow rate. Since the density may change, we cannot assume that $u_{out} = \sum_{p=1}^{P} u_p$.

The equation for temperature (1.12) also needs to be modified in order to account for the convective energy flows.

Firstly, the total convective internal energy flow (W) entering the reactor through the P input streams is given by

$$\sum_{p=1}^{P} \rho^p e^p u^p = \sum_{p=1}^{P} \rho^p \Big(\sum_{i=1}^{N} Y_i^p \hat{e}_i(\theta^p) \Big) u^p = \sum_{p=1}^{P} \Big(\sum_{i=1}^{N} \mathcal{M}_i W_i^p \hat{e}_i(\theta^p) \Big) u^p,$$

because $\rho^p Y_i^p = \mathcal{M}_i W_i^p$. Similarly, the convective energy flow exiting the reactor (W) is given by

$$\rho e u_{out} = u_{out} \sum_{i=1}^{N} \mathcal{M}_i y_i \hat{e}_i(\theta).$$

Secondly, (1.9) has to be modified as follows:

$$\begin{aligned} \frac{d(V\rho e)}{dt} &= \sum_{i=1}^{N} \mathcal{M}_i \Big(\frac{d(Vy_i)}{dt} e_i + V y_i \frac{de_i}{dt} \Big) \\ &= V \sum_{i=1}^{N} \mathcal{M}_i \Big(e_i \big[A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) + \frac{1}{V} W\mathbf{u} - \frac{1}{V} \mathbf{y} u_{out} \big]_i + y_i \hat{c}_i(\theta) \frac{d\theta}{dt} \Big), \end{aligned} \tag{1.15}$$

where $e_i = \hat{e}_i(\theta)$. Thirdly, equation (1.8) has to be replaced by

$$\frac{d(V\rho e)}{dt} = g(\theta_{ext} - \theta) + \sum_{p=1}^{P} \Big(\sum_{i=1}^{N} \mathcal{M}_i W_i^p \hat{e}_i(\theta^p) \Big) u^p - u_{out} \sum_{i=1}^{N} \mathcal{M}_i y_i \hat{e}_i(\theta). \tag{1.16}$$

By subtracting (1.15) from (1.16) and then dividing by V, we get the equation replacing (1.11):

$$\rho c \frac{d\theta}{dt} = -\Delta\hat{\mathbf{H}}(\theta) \cdot \hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) + \frac{g}{V}(\theta_{ext} - \theta) + \frac{1}{V} \sum_{p=1}^{P} \Big(\sum_{i=1}^{N} \mathcal{M}_i W_i^p \big(\hat{e}_i(\theta^p) - \hat{e}_i(\theta) \big) \Big) u^p.$$

Dividing by ρc we finally get

$$\frac{d\theta}{dt} = - \frac{\Delta\hat{\mathbf{H}}(\theta) \cdot \hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) - \frac{g}{V}(\theta_{ext} - \theta) - \frac{1}{V} \sum_{p=1}^{P} \Big(\sum_{i=1}^{N} \mathcal{M}_i W_i^p \big(\hat{e}_i(\theta^p) - \hat{e}_i(\theta) \big) \Big) u^p}{\mathbf{w}'(\theta) \cdot \mathbf{y}}.$$

Let us notice that if there is no change of state then

$$\hat{e}_i(\theta^p) - \hat{e}_i(\theta) = \int_{\theta}^{\theta_p} c_{vi}(s)\, ds.$$

Now, let us assume that the density of the reacting mixture does not depend either on the composition or on the temperature. Then the volume only changes due to input and output flows and the equations giving the volume are the following:

$$\frac{dV}{dt}(t) = \sum_{p=1}^{P} u^p(t) - u_{out}(t), \tag{1.17}$$

$$V(0) = V_0. \tag{1.18}$$

In this case we have

$$\frac{d(V\mathbf{y})}{dt} = V\frac{d\mathbf{y}}{dt} + \frac{dV}{dt}\mathbf{y} = V\frac{d\mathbf{y}}{dt} + \mathbf{y}\Big(\sum_{p=1}^{P} u^p(t) - u_{out}(t)\Big)$$

and since we use equations (1.17) for the volume, we can write the model in terms of $\mathbf{y}$ as follows:

$$\frac{dV}{dt} = \sum_{p=1}^{P} u^p - u_{out},$$

$$\frac{d\mathbf{y}}{dt} = A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) + \frac{1}{V}W\mathbf{u} - \frac{1}{V}\mathbf{y}\sum_{p=1}^{P} u^p,$$

$$\frac{d\theta}{dt} = -\frac{\Delta\hat{\mathbf{H}}(\theta)\cdot\hat{\boldsymbol{\delta}}(\theta,\mathbf{y}) - \frac{g}{V}(\theta_{ext}-\theta) - \frac{1}{V}\sum_{p=1}^{P}\Big(\sum_{i=1}^{N}\mathcal{M}_i W_i^p\big(\hat{e}_i(\theta^p) - \hat{e}_i(\theta)\big)\Big)u^p}{\mathbf{w}'(\theta)\cdot\mathbf{y}},$$

$$V(0) = V_0,$$

$$\mathbf{y}(0) = \mathbf{y}_0,$$

$$\theta(0) = \theta_0.$$

1.3.2 Steady-state CSTR model

Let us assume that the outside temperature and the input flows are time independent. Then the CSTR may attain a steady-state.

Assuming also that the mixture density is independent of composition and temperature, then the volume of the mixture is constant and equal to the initial one which is supposed to be given. Then the model is the following non-linear system of numerical equations:

$$A\hat{\boldsymbol{\delta}}(\theta,\mathbf{y})+\frac{1}{V}(W\mathbf{u}-u_{out}\mathbf{y})=\mathbf{0},$$

$$\Delta\hat{\mathbf{H}}(\theta)\cdot\hat{\boldsymbol{\delta}}(\theta,\mathbf{y})-\frac{g}{V}(\theta_{ext}-\theta)-\frac{1}{V}\sum_{p=1}^{P}\Big(\sum_{i=1}^{N}\mathcal{M}_iW_i^p\big(\hat{e}_i(\theta^p)-\hat{e}_i(\theta)\big)\Big)u^p=0.$$

Remark 1.3.1. *Let us notice that the energy equation has the same form for the constant and variable density cases. Moreover, by using (1.16) it can also be written as*

$$g(\theta_{ext}-\theta)+\sum_{p=1}^{P}\Big(\sum_{i=1}^{N}\mathcal{M}_iW_i^p\hat{e}_i(\theta^p)\Big)u^p-u_{out}\sum_{i=1}^{N}\mathcal{M}_iy_i\hat{e}_i(\theta)=0.$$

Chapter 2

Modelling $n-$dimensional convection-diffusion-reaction systems

Mathematical models for heat and mass transfer in this type of reactors are usually called in the literature convection-reaction-diffusion systems. In this sense, the term convection-reaction-diffusion systems refers to models which produce locally transformations of chemical species by chemical reactions and at the same time are transported in the reactor by convection and diffusion. They appear obviously in chemical engineering, but they have been used in the study of different phenomena in biology, geology or physics.

We study this type of reactors in a general mathematical framework. In the next chapters we will first prove a theorem of existence of solution and then we will address the numerical analysis by using finite element methods which will include error estimates.

2.1 Modelling the convection-diffusion-reaction system

Let us consider Ω an open bounded set in $\mathbb{R}^n$ with smooth boundary $\partial\Omega$, as represented in Figure 2.1, and let ν be the outward unit normal vector to $\partial\Omega$. Moreover, let Γ_1 denote the reactor inlet boundary, Γ_2 the reactor outlet and Γ_3 the reactor wall.

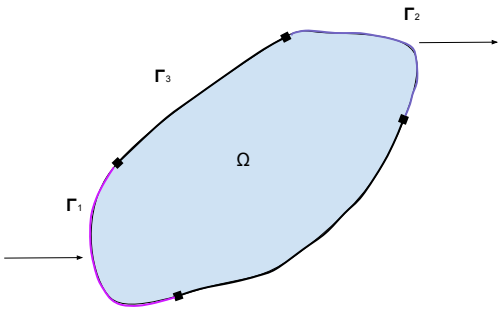

Figure 2.1: $n-$dimensional domain with bounds

Let $\mathbf{y}(t,x)$ (mol/m^3) be the vector of species concentrations involved in the reactions, where $(t,x) \in (0,T) \times \Omega$. Then, the mass balance of species leads to the following system of partial differential equations (see (A.1)):

$$\frac{\partial \mathbf{y}}{\partial t} + \nabla \mathbf{y}\mathbf{v} - D\Delta \mathbf{y} = \boldsymbol{\varphi}, \tag{2.1}$$

where

- $\mathbf{v}$ (m/s) is the (given) velocity. We consider the case of an incompressible fluid and hence div $\mathbf{v} = 0$. We also assume that $\mathbf{v}$ is time independent.
- D (m^2/s) is the diagonal matrix of the diffusion coefficients of species which are assumed constant and strictly positive.
- $\boldsymbol{\varphi}(t,x,\mathbf{y},\theta)$ (mol/(m^3 s)) denotes the source term also called reaction term. More precisely, it represents the vector of reaction rates described in Section 1.1.2 and corresponding to the law of mass action, multiplied to the left by the stoichiometric matrix A.

Similarly, the general energy conservation equation for the fluid bulk can be written as follows (see (A.4)):

$$\frac{\partial(\rho e)}{\partial t} + \mathrm{div}(\rho e \mathbf{v}) + \mathrm{div}\mathbf{q} = 0, \tag{2.2}$$

where

- ρ (kg/m^3) is density of the mixture,
- e (J/kg) is the specific internal energy of the bulk fluid,

- $\mathbf{q}$ (W/(m^2) is the heat flux vector given by Fourier's law $\mathbf{q} = -k \operatorname{grad}\theta$,
- k (W/(mK)) is the effective coefficient of thermal conductivity.

Let us recall that

$$e = \sum_{i=1}^{N} Y_i e_i,$$

where Y_i denotes the mass fraction of species E_i which is related to its concentration by

$$\rho Y_i = \mathcal{M}_i y_i$$

and the specific internal energy of species E_i depends on temperature: $e_i = \hat{e}_i(\theta)$. Hence,

$$\rho e = \sum_{i=1}^{N} \rho Y_i e_i = \sum_{i=1}^{N} \mathcal{M}_i y_i e_i$$

and then

$$\frac{\partial(\rho e)}{\partial t} = \sum_{i=1}^{N} \mathcal{M}_i \left(e_i \frac{\partial y_i}{\partial t} + y_i \frac{\partial e_i}{\partial t} \right). \tag{2.3}$$

Similarly,

$$\operatorname{div}(\rho e \mathbf{v}) = \rho e \operatorname{div}\mathbf{v} + \mathbf{v} \cdot \nabla(\rho e) = \mathbf{v} \cdot \nabla(\rho e) = \sum_{i=1}^{N} \mathcal{M}_i \left(e_i \nabla y_i \cdot \mathbf{v} + y_i \nabla e_i \cdot \mathbf{v} \right). \tag{2.4}$$

By adding (2.3) and (2.4) we obtain

$$\begin{aligned} &\frac{\partial(\rho e)}{\partial t} + \nabla(\rho e) \cdot \mathbf{v} \\ &= \sum_{i=1}^{N} \mathcal{M}_i e_i \left(\frac{\partial y_i}{\partial t} + \nabla y_i \cdot \mathbf{v} \right) + \sum_{i=1}^{N} \mathcal{M}_i y_i \left(\frac{\partial e_i}{\partial t} + \nabla e_i \cdot \mathbf{v} \right) \\ &= \sum_{i=1}^{N} \hat{w}_i(\theta) \left(\frac{\partial y_i}{\partial t} + \nabla y_i \cdot \mathbf{v} \right) + \sum_{i=1}^{N} \mathcal{M}_i y_i \hat{c}_{vi}(\theta) \left(\frac{\partial \theta}{\partial t} + \nabla \theta \cdot \mathbf{v} \right), \end{aligned} \tag{2.5}$$

where $\hat{c}_{vi}(\theta)$ is the specific heat at constant volume of the i-th species and $\hat{w}_i(\theta)$ is defined in (2.22). Let us recall that the specific heat at constant volume of the mixture is defined by

$$\hat{c}_v(\theta) = \sum_{i=1}^{N} Y_i \hat{c}_{vi}(\theta)$$

and hence,

$$\sum_{i=1}^{N} \mathcal{M}_i y_i \hat{c}_{vi}(\theta) = \rho \sum_{i=1}^{N} Y_i \hat{c}_{vi}(\theta) = \rho \hat{c}_v(\theta).$$

By using (2.1) and the previous equality we get

$$\frac{\partial(\rho e)}{\partial t} + \nabla(\rho e) \cdot \mathbf{v} = \hat{\mathbf{w}}(\theta) \cdot [D\Delta \mathbf{y} + \boldsymbol{\varphi}] + \rho \hat{c}_v(\theta) \left(\frac{\partial \theta}{\partial t} + \nabla \theta \cdot \mathbf{v} \right). \tag{2.6}$$

The mass diffusion term in the previous equation can be neglected against the source terms $\boldsymbol{\varphi}$. Thus, the energy equation (2.2) can be finally written as

$$\rho \hat{c}_v(\theta) \big(\frac{\partial \theta}{\partial t} + \nabla \theta \cdot \mathbf{v} \big) - k\Delta\theta = -\hat{\mathbf{w}}(\theta) \cdot \boldsymbol{\varphi}. \tag{2.7}$$

2.1.1 Boundary conditions

The boundary conditions are imposed on the boundary of the reactor.

- Reactor entrance (Γ_1).

  1. Mass:

  $$D \frac{\partial \mathbf{y}}{\partial \boldsymbol{\nu}}(t,x) - (\mathbf{v}(x) \cdot \boldsymbol{\nu}(x)) \mathbf{y}(t,x) = \mathbf{g}(t,x), \quad (t,x) \in (0,T) \times \Gamma_1, \tag{2.8}$$

  where $\mathbf{g}$ (mol/(m$^2 s$) is an enough smooth function, representing the molar flux os species entering the reactor at time t and position x.

  2. Energy:

  $$\theta(t,x) = \theta_{in}(t), \quad (t,x) \in (0,T) \times \Gamma_1. \tag{2.9}$$

- Reactor exit (Γ_2).

  1. Mass:

  $$D \frac{\partial \mathbf{y}}{\partial \boldsymbol{\nu}}(t,x) = \mathbf{0}, \quad (t,x) \in (0,T) \times \Gamma_2. \tag{2.10}$$

  2. Energy:

  $$k \frac{\partial \theta}{\partial \boldsymbol{\nu}}(t,x) = 0, \quad (t,x) \in (0,T) \times \Gamma_2. \tag{2.11}$$

- Reactor walls (Γ_3).

  1. Mass:

  $$D \frac{\partial \mathbf{y}}{\partial \boldsymbol{\nu}}(t,x) = \mathbf{0}, \quad (t,x) \in (0,T) \times \Gamma_3. \tag{2.12}$$

2. Energy:

$$k\frac{\partial\theta}{\partial\boldsymbol{\nu}}(t,x) = h_{ext}\Big(\theta_{ext}(t) - \theta(t,x)\Big), \quad (t,x) \in (0,T)\times\Gamma_3, \quad (2.13)$$

where h_{ext} (W/(m^{2}K)) is a heat transfer coefficient between the reactants and the exterior of the reactor and θ_{ext} denotes the temperature of the latter.

2.1.2 Initial conditions

1. Mass:

$$\mathbf{y}(0,x) = \mathbf{y}_0(x). \quad (2.14)$$

2. Energy:

$$\theta(0,x) = \theta_0(x). \quad (2.15)$$

2.1.3 The full n-dimensional model

Finally, the full model for a $n-$ dimensional convection-diffusion-reaction system can be writen as:

$$\begin{aligned}
\frac{\partial\mathbf{y}}{\partial t} + \nabla\mathbf{y}\mathbf{v} - D\Delta\mathbf{y} &= \boldsymbol{\varphi},\\
\rho\hat{c}_v(\theta)\big(\frac{\partial\theta}{\partial t} + \nabla\theta\cdot\mathbf{v}\big) - k\Delta\theta &= -\hat{\mathbf{w}}(\theta)\cdot\boldsymbol{\varphi},\\
D\frac{\partial\mathbf{y}}{\partial\boldsymbol{\nu}}(t,x) - (\mathbf{v}(x)\cdot\boldsymbol{\nu}(x))\mathbf{y}(t,x) &= \mathbf{g}(t,x), \quad (t,x)\in(0,T)\times\Gamma_1,\\
\theta(t,x) &= \theta_{in}(t), \quad (t,x)\in(0,T)\times\Gamma_1,\\
D\frac{\partial\mathbf{y}}{\partial\boldsymbol{\nu}}(t,x) &= \mathbf{0}, \quad (t,x)\in(0,T)\times\Gamma_2,\\
k\frac{\partial\theta}{\partial\boldsymbol{\nu}}(t,x) &= 0, \quad (t,x)\in(0,T)\times\Gamma_2,\\
D\frac{\partial\mathbf{y}}{\partial\boldsymbol{\nu}}(t,x) &= \mathbf{0}, \quad (t,x)\in(0,T)\times\Gamma_3,\\
k\frac{\partial\theta}{\partial\boldsymbol{\nu}}(t,x) &= h_{ext}\Big(\theta_{ext}(t) - \theta(t,x)\Big), \quad (t,x)\in(0,T)\times\Gamma_3,\\
\mathbf{y}(0,x) = \mathbf{y}_0(x), &\qquad \theta(0,x) = \theta_0(x).
\end{aligned}$$

2.2 A particular one-dimensional reactor: the Plug Flow Reactor (PFR)

Plug flow reactors are also called ***continuous tubular reactors*** and ***piston flow reactors***. What does *plug flow* mean? In principle, due to viscosity, the velocity of the flow in a pipe is null on the wall. Moreover, in the laminar regime, the velocity profile is parabolic with the maximum at the central axis of the pipe. The plug flow is a simple model where the velocity is assumed to be constant on any cross-section of the pipe (but it may depend on time).

In order to write a model for a transient PFR the conservation equations (see Appendix A) are integrated on the cross-sections of the pipe leading to a one-dimensional model. Let z be the axial coordinate of the reactor of length L. Then $z \in [0, L]$.

We make the following assumptions:

- All thermodynamic magnitudes depend only on z and t.
- Velocity: $\mathbf{v} = v_z \mathbf{e}_z$ with v_z independent of x and y (plug flow assumption). In what follows we drop subscript z from v_z.
- The conductive term can be neglected, namely, term $T_v \cdot D$ is dropped out of the equations.
- There is no external volumetric heat source, i.e., $f = 0$.

2.2.1 Transient Plug Flow Reactors

In general, the mixture is not incompressible and the velocity may depend on z and t. But we work with constant density. In this case we assume that the initial density of the mixture in the reactor is a constant function (i.e., homogeneous) and equal to the density of the input mixture which is then also constant along the time. From the mass conservation equation (A.2) we deduce that the mixture is incompressible, i.e., $\mathrm{div}\mathbf{v} = 0$ which in the present case means $\dfrac{\partial v_z}{\partial z} = 0$, then v_z is independent of z, thus $v_z = v(t)$ (in what follows we drop subscript z for the sake of simplicity). Therefore, in this case $v(t)$ is supposed to be given (in fact, it is the velocity of the input current at the inlet of the reactor which can be obtained from its volumetric flow rate dividing by the area of the reactor cross-section). Hence, neither the motion equation nor the state equation are needed.

We can see the illustration of the reactor below:

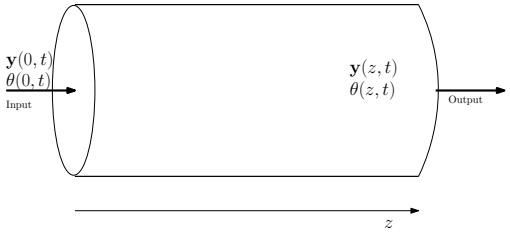

Figure 2.2: Plug Flow Reactor

Species mass conservation

By dividing by the molecular mass $\mathcal{M}_i$ and introducing the concentration of species,

$$y_i = \frac{\rho Y_i}{\mathcal{M}_i},$$

equations (A.1) can be rewritten. In reactors of this type, the diffusion is usually neglected. However, in industrial reactors although the convection term predominate, diffusion also occurs, so we have

$$\frac{\partial y_i}{\partial t} + \frac{\partial (y_i v)}{\partial z} - d_i \frac{\partial^2 y_i}{\partial z^2} = \sum_{j=1}^{R} a_{ij} \delta_j(\theta, \mathbf{y}), \ i = 1, ..., N, \tag{2.16}$$

because fields only depend on z and t. (2.16) can be written in a more compact form as

$$\frac{\partial \mathbf{y}}{\partial t} + \frac{\partial (\mathbf{y} v)}{\partial z} - D \frac{\partial^2 \mathbf{y}}{\partial z^2} = A \hat{\boldsymbol{\delta}}(\theta, \mathbf{y}). \tag{2.17}$$

Energy equation

Firstly, the specific (i.e., per unit mass) internal energy of the i-th species is given by

$$e_i(z,t) = \hat{e}_i(\theta(z,t)),$$

with

$$\hat{e}_i(\theta) := e_i^* + \int_{\theta^*}^{\theta} \hat{c}_i(s)\, ds,$$

where e_i^* is the internal energy of formation of the i-th species at temperature θ^* and $c_i = \hat{c}_i(\theta)$ is the specific heat of the i-th species $(J/(kgK))$ at temperature θ. For the mixture we have

$$e = \sum_{i=1}^{N} Y_i e_i$$

and hence,

$$\rho e = \sum_{i=1}^{N} \rho Y_i e_i = \sum_{i=1}^{N} \mathcal{M}_i y_i e_i.$$

Therefore,

$$\begin{aligned} &\frac{\partial(\rho e)}{\partial t} + \frac{\partial(\rho v e)}{\partial z} = \sum_{i=1}^{N} \mathcal{M}_i \big(\frac{\partial(y_i e_i)}{\partial t} + \frac{\partial(y_i e_i v)}{\partial z}\big) \\ &= \sum_{i=1}^{N} \mathcal{M}_i e_i \big(\frac{\partial y_i}{\partial t} + \frac{\partial(y_i v)}{\partial z}\big) + \sum_{i=1}^{N} \mathcal{M}_i y_i \big(\frac{\partial e_i}{\partial t} + v\frac{\partial e_i}{\partial z}\big). \end{aligned} \tag{2.18}$$

From the definition of specific heat, the chain rule yields

$$\frac{\partial e_i}{\partial t} = c_i \frac{\partial \theta}{\partial t}, \qquad \frac{\partial e_i}{\partial z} = c_i \frac{\partial \theta}{\partial z}.$$

By using these equalities and (2.16) we get

$$\frac{\partial(\rho e)}{\partial t} + \frac{\partial(\rho v e)}{\partial z} = \sum_{i=1}^{N} \mathcal{M}_i e_i \big(A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) + D\frac{\partial^2 \mathbf{y}}{\partial z^2}\big)_i + \sum_{i=1}^{N} \mathcal{M}_i y_i c_i \big(\frac{\partial \theta}{\partial t} + v\frac{\partial \theta}{\partial z}\big). \tag{2.19}$$

Moreover, let c be the specific heat of the mixture defined by

$$c := \sum_{i=1}^{N} Y_i c_i.$$

We have

$$\rho c = \sum_{i=1}^{N} \mathcal{M}_i y_i c_i. \tag{2.20}$$

Let us assume that the reactor is adiabatic, i.e., there is no heat exchange with the exterior. Thus, by using (2.19), the energy equation (A.4) becomes

$$\rho c\frac{\partial \theta}{\partial t} + \rho c v\frac{\partial \theta}{\partial z} - k\frac{\partial^2 \theta}{\partial z^2} = -\hat{\mathbf{w}}(\theta)\cdot A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) = -A^t\hat{\mathbf{w}}(\theta)\cdot\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) = -\Delta\hat{\mathbf{H}}(\theta)\cdot\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}), \tag{2.21}$$

where the components of vector $\hat{\mathbf{w}}(\theta) \in \mathbb{R}^N$ are defined by

$$\hat{w}_i(\theta) = \mathcal{M}_i \hat{e}_i(\theta) \quad (J/mol) \tag{2.22}$$

and the components of the L-dimensional vector

$$\Delta\hat{\mathbf{H}}(\theta) := A^t \hat{\mathbf{w}}(\theta) \quad (J/mol)$$

are the ***heat of the reactions*** at temperature θ. We have,

$$\Delta\hat{H}_l(\theta) = \sum_{i=1}^{N} (\lambda_i^l - \nu_i^l)\mathcal{M}_i \hat{e}_i(\theta).$$

Summarizing, the energy conservation equation for an adiabatic transient PFR is the following nonlinear partial differential equation system:

$$\rho c\left(\frac{\partial \theta}{\partial t} + v\frac{\partial \theta}{\partial z}\right) - k\frac{\partial^2 \theta}{\partial z^2} = -\Delta\hat{\mathbf{H}}(\theta) \cdot \hat{\boldsymbol{\delta}}(\theta, \mathbf{y}), \tag{2.23}$$

with

$$\rho c = \hat{\mathbf{w}}'(\theta) \cdot \mathbf{y}. \tag{2.24}$$

Boundary conditions

Let us notice that the above partial differential equations are of first order both in time and space. Hence, one boundary condition has to be prescribed for each of them. If $v(0,t) > 0$ composition and temperature have to be provided at point $z = 0$:

$\mathbf{y}(0,t)$ given, $t \in (0,T)$,

$\theta(0,t)$ given, $t \in (0,T)$.

Initial conditions

The following initial conditions has to be given:

- $\mathbf{y}(z,0)$, $z \in (0,L)$,
- $\theta(z,0)$, $z \in (0,L)$.

The non-adiabatic case

In the above models we have assumed that the reactor is thermally isolated, so there is no heat exchange with the exterior. In this case we say that the PFR is adiabatic.

Now, let us consider the case where the reactor exchanges heat with its surroundings according to the Newton convection law. This means that the reactor heat loss per unit surface and time is given by

$$h\,(\theta - \theta_\infty) \quad (W/m^2), \tag{2.25}$$

where h $(W/(m^2K))$ is a convective heat transfer coefficient depending on the outside cooling (e.g., natural convection, forced convection, ...) and $\theta_{ext}(z,t)$ (K) is the outside temperature. If the reactor is a cylinder with radius R, then the energy equation (2.23) must be replaced by the following one:

$$\rho c\Big(\frac{\partial \theta}{\partial t} + v\frac{\partial \theta}{\partial z}\Big) - k\frac{\partial^2 \theta}{\partial z^2} = -\Delta\hat{\mathbf{H}}(\theta)\cdot\hat{\boldsymbol{\delta}}(\theta,\mathbf{y}) + \frac{2\pi Rh}{\pi R^2}\,(\theta_{ext} - \theta). \tag{2.26}$$

Thus, the full model for a non-adiabatic PFR in transient state with constant density is

$$\frac{\partial \mathbf{y}}{\partial t} + v\frac{\partial \mathbf{y}}{\partial z} - D\frac{\partial^2 \mathbf{y}}{\partial z^2} = A\hat{\boldsymbol{\delta}}(\theta,\mathbf{y}),$$

$$(\hat{\mathbf{w}}'(\theta)\cdot\mathbf{y})\left(\frac{\partial \theta}{\partial t} + v\frac{\partial \theta}{\partial z}\right) - k\frac{\partial^2 \theta}{\partial z^2} = -\Delta\hat{\mathbf{H}}(\theta)\cdot\hat{\boldsymbol{\delta}}(\theta,\mathbf{y}) + \frac{2h}{R}\,(\theta_{ext} - \theta),$$

$$\mathbf{y}(0,t) \text{ and } \theta(0,t) \text{ are given},$$

$$D\frac{\partial \mathbf{y}}{\partial z}(t,L) = \mathbf{0},$$
$$k\frac{\partial \theta}{\partial z}(t,L) = 0,$$

$$\mathbf{y}(z,0) = \mathbf{y}^0(z), \quad \theta(z,0) = \theta^0(z).$$

2.2.2 Steady-state PFR

In this case the thermodynamic magnitudes do not depend on time, so partial derivatives with respect to time disappear from model. We also assume constant density.

$$v\frac{d\mathbf{y}}{dz} - D\frac{\partial^2 \mathbf{y}}{\partial z^2} = A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}),$$

$$(\hat{\mathbf{w}}'(\theta)\cdot\mathbf{y})v\frac{\partial\theta}{\partial z} - k\frac{\partial^2\theta}{\partial z^2} = -\Delta\hat{\mathbf{H}}(\theta)\cdot\hat{\boldsymbol{\delta}}(\theta,\mathbf{y}) + \frac{2h}{R}(\theta_{ext}-\theta),$$

$\mathbf{y}(0)$ and $\theta(0)$ are given.

Remark 2.2.1. *Notice that if the diffusion terms are neglected, the above model is similar to the one corresponding to a batch STR. Indeed, by making the change of variable,*

$$t = \frac{z}{v},$$
$$\frac{d}{dz} = \frac{1}{v}\frac{d}{dt},$$

the above equations and boundary conditions yield the following initial-value problem:

$$\frac{d\mathbf{y}}{dt} = A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}),$$

$$\frac{d\theta}{dt} = -\frac{1}{\hat{\mathbf{w}}'(\theta)\cdot\mathbf{y}}\Big(-\Delta\hat{\mathbf{H}}(\theta)\cdot\hat{\boldsymbol{\delta}}(\theta,\mathbf{y}) + \frac{2h}{R}(\theta_\infty-\theta)\Big),$$

$\mathbf{y}(0)$ *and* $\theta(0)$ *are given.*

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Chapter 3

Modelling catalytic fixed bed reactors (FBR)

In this chapter we derive the model for ***fixed bed reactors***, also called ***packed bed reactors*** (PBR) or ***packed bed catalytic reactors***. We focus the study in the continuum models which are frequently used in important industrial processes. Some of them are the ethylene oxidation and the oxidation of methanol to formaldehyde. Despite of the existence of newer type of reactors such as fluidized bed reactors, the packed bed reactors are extensively used for both large scale processing in petroleum and basic chemical industry.

In fact, in industry a bundle of tubes filled with catalyst is considered, usually arranged within a large reactor shell. In these terms, it is assumed that the temperature in the tube remains constant and that the conditions are equal in each tube (there is a fluid around the tubes to keep an adequate temperature). But this does not happen in practice, where the reactions may have a significant effect on the reactor.

In our framework, the term "packed bed reactor" is related to a single cylindrical shell with convex heads with a packed bed of catalytic particles of uniform size, which are immobilized or fixed within the tube. A fluid mixture of reactants is introduced at the reactor entrance which moves along the reactor and interacts with the catalytic active particles; the reactions usually produce heat exchanges. If it is necessary, the temperature is regulated through the wall of the tube.

We consider FBRs as heterogeneous reactors. Plug-flow is assumed, i.e., $\mathbf{v} = v\mathbf{e}_z$, where z is the axial direction.

The model for these reactors is based on the conservation laws for mass, energy and momentum, and leads to partial differential equations. Due to the complexity of the system, the description of packed bed reactors must be sim-

plified. For this reason, there are different valid packed bed reactor models. In fact, each problem should be analyzed to do the adequate simplifying assumptions. In some cases, the reactor can be considered as pseudo-homogeneous. If the differences between the fluid and solid phases are significant, heterogeneous models have to be considered. Moreover, sometimes intra-particle resistance should be taken into account.

We consider a multi-scale model. The bed is modelled at the micro-scale level as a continuum of small particles of solid material containing the catalyst and interacting with the fluid. In what follows we will assume these particles spherical, but other geometries as cylinder or slab can be considered by straightforward modifications in the model. The fluid bulk is modelled at the macro-scale level as a fluid flowing in a porous media. For the macro-scale model, the effect of the micro-scale is represented by source terms both in the species concentration equations and in the energy equation. In its turn, the micro-scale model is coupled to the macro-scale magnitudes through boundary conditions.

In what follows, we denote with superscript f the magnitudes for the macro-scale and by superscript s those for the micro-scale. We assume that all fields have cylindrical symmetry in the macro-scale. Thus, we write the equations in cylindrical coordinates in order to exploit this fact by reducing the spatial dimension. We denote by r the radial coordinate and by z the axial one. We also assume that inside the spherical particles all fields have spherical symmetry, i.e., their spatial dependence is only through the radial variable which will be denoted by r_s. Summarizing, we propose below a heterogeneous model which assumes that the chemical reactions take place both in the fluid bulk and inside the particles at the micro-scale level.

In order to visualize the above description of the reactor we show a diagram in Figure 3.1.

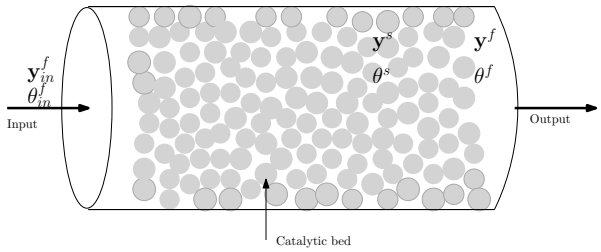

Figure 3.1: Fixed bed reactor

3.1 Modelling the macro-scale (fluid bulk)

We assume cylindrical symmetry in the macro-scale. Then, the following domain is considered:

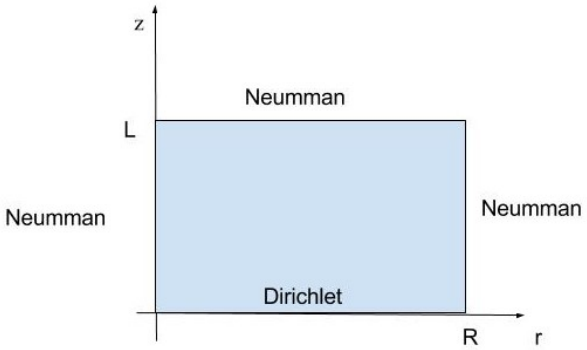

Figure 3.2: Macro-scale domain

Let us denote by $\varepsilon^f(r,z,t)$ the bed porosity at point (r,z) in the reactor and at time t, i.e., the volume occupied by the fluid per unit reactor volume. If the field of concentrations in the fluid is $\mathbf{y}^f(r,z,t)$ (mol/m^3), then the concentrations with respect to the total volume of the reactor will be $\varepsilon^f(r,z,t)\mathbf{y}^f(r,z,t)$ (mol/m^3) and the mass conservation equations of species become (see (A.1)),

$$\begin{aligned}&\frac{\partial}{\partial t}(\varepsilon^f\mathbf{y}^f)+\frac{\partial}{\partial z}(\varepsilon^f\mathbf{y}^f v)-\frac{1}{r}\frac{\partial}{\partial r}\Big(D_r^f r\frac{\partial}{\partial r}(\varepsilon^f\mathbf{y}^f)\Big)-\frac{\partial}{\partial z}\Big(D_z^f\frac{\partial}{\partial z}(\varepsilon^f\mathbf{y}^f)\Big)\\&=A^f\boldsymbol{\delta}^f(\theta^f,\mathbf{y}^f)+\mathbf{g},\end{aligned}\tag{3.1}$$

where

- v (m/s) is the (given) axial velocity. We consider the case of an incompressible fluid so, div$\mathbf{v}=\dfrac{\partial v}{\partial z}=0$ and hence v cannot depend on z: $v=v(r,t)$).
- D_r^f and D_z^f (m^2/s) are diagonal matrices containing the diffusion coefficients of species (this case corresponds to a particular orthotropic diffusion being r and z the principal directions, but other anisotropic cases could be easily considered).
- $\mathbf{g}(r,z,t)$ (mol/(m^3 s)) denotes the amount of substance of species per unit of reactor volume and time provided by the solid phase to the liquid

bulk at point (r, z) and time t. It will be computed from the micro-scale model for the solid phase.

Similarly, neglecting viscous dissipation, the general energy conservation equation for the fluid bulk can be written as follows (see (A.4)):

$$\frac{\partial(\varepsilon^f \rho^f e^f)}{\partial t} + \frac{\partial(\varepsilon^f \rho^f e^f v)}{\partial z} + \mathrm{div}\mathbf{q}^f = f, \tag{3.2}$$

where

- ρ^f (kg/m^3) is the density of the bulk fluid,
- e^f (J/kg) is the specific internal energy of the bulk fluid,
- $\mathbf{q}^f$ (W/(m^2) is the heat flux vector given by Fourier's law $\mathbf{q}^f = -k^f \mathrm{grad}\,\theta^f$,
- k^f (W/(mK)) is the diagonal matrix of effective coefficient of thermal conductivities in radial and axial directions, k_r^f and k_z^f, respectively. The same remark as for mass diffusion can be made.
- f (W/m^3) denotes the heat per unit of reactor volume and time provided by the solid phase to the liquid bulk. It will be computed from the micro-scale model.

Let us write (3.2) in cylindrical coordinates. Assuming axisymmetry it becomes

$$\frac{\partial(\varepsilon^f \rho^f e^f)}{\partial t} + \frac{\partial(\varepsilon^f \rho^f e^f v)}{\partial z} - \frac{1}{r}\frac{\partial}{\partial r}\Big(k_r^f r \frac{\partial \theta^f}{\partial r}\Big) - \frac{\partial}{\partial z}\Big(k_z^f \frac{\partial \theta^f}{\partial z}\Big) = f. \tag{3.3}$$

Let us recall that

$$e^f = \sum_{i=1}^{N} Y_i^f e_i^f,$$

where Y_i^f denotes the mass fraction of species E_i which is related to its concentration by

$$\rho^f Y_i^f = \mathcal{M}_i y_i^f$$

and the specific internal energy of species E_i depends on temperature: $e_i^f = \hat{e}_i(\theta^f)$. Hence,

$$\rho^f e^f = \sum_{i=1}^{N} \rho^f Y_i^f e_i^f = \sum_{i=1}^{N} \mathcal{M}_i y_i^f e_i^f$$

and then

$$\frac{\partial(\varepsilon^f \rho^f e^f)}{\partial t} = \sum_{i=1}^{N} \mathcal{M}_i \big(e_i^f \frac{\partial(\varepsilon^f y_i^f)}{\partial t} + \varepsilon^f y_i^f \frac{\partial e_i^f}{\partial t}\big). \tag{3.4}$$

Similarly

$$\frac{\partial(\varepsilon^f \rho^f e^f v)}{\partial z} = \sum_{i=1}^{N} \mathcal{M}_i \big(e_i^f \frac{\partial(\varepsilon^f y_i^f v)}{\partial z} + \varepsilon^f v y_i^f \frac{\partial e_i^f}{\partial z}\big). \tag{3.5}$$

By adding (3.4) and (3.5) we obtain

$$\begin{aligned}
&\frac{\partial(\varepsilon^f \rho^f e^f)}{\partial t} + \frac{\partial(\varepsilon^f \rho^f e^f v)}{\partial z} \\
&= \sum_{i=1}^{N} \mathcal{M}_i e_i^f \big(\frac{\partial(\varepsilon^f y_i^f)}{\partial t} + \frac{\partial(\varepsilon^f y_i^f v)}{\partial z}\big) + \varepsilon^f \sum_{i=1}^{N} \mathcal{M}_i y_i^f \big(\frac{\partial e_i^f}{\partial t} + v \frac{\partial e_i^f}{\partial z}\big) \\
&= \sum_{i=1}^{N} \hat{w}_i(\theta^f) \big(\frac{\partial(\varepsilon^f y_i^f)}{\partial t} + \frac{\partial(\varepsilon^f y_i^f v)}{\partial z}\big) + \varepsilon^f \sum_{i=1}^{N} \mathcal{M}_i y_i^f \hat{c}_{vi}^f(\theta^f) \big(\frac{\partial \theta^f}{\partial t} + v \frac{\partial \theta^f}{\partial z}\big),
\end{aligned} \tag{3.6}$$

where $\hat{c}_{vi}(\theta^f)$ is the specific heat at constant volume of the i-th species and $\hat{w}_i(\theta^f)$ has been defined in (2.22). Let us recall that the specific heat at constant volume of the mixture is defined by

$$\hat{c}_v^f(\theta^f) = \sum_{i=1}^{N} Y_i^f \hat{c}_{vi}(\theta^f)$$

and hence,

$$\sum_{i=1}^{N} \mathcal{M}_i y_i^f \hat{c}_{vi}(\theta^f) = \rho^f \sum_{i=1}^{N} Y_i^f \hat{c}_{vi}(\theta^f) = \rho^f \hat{c}_v^f(\theta^f).$$

By using (3.1) and the previous equality we get

$$\begin{aligned}
&\frac{\partial(\varepsilon^f \rho^f e^f)}{\partial t} + \frac{\partial(\varepsilon^f \rho^f e^f v)}{\partial z} \\
&= \hat{\mathbf{w}}(\theta^f) \cdot \left[\frac{1}{r}\frac{\partial}{\partial r}\Big(D_r^f r \frac{\partial}{\partial r}(\varepsilon^f \mathbf{y}^f)\Big) + \frac{\partial}{\partial z}\Big(D_z^f \frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f)\Big)\right) + A^f \boldsymbol{\delta}^f + \mathbf{g}\Big] \\
&+ \varepsilon^f \rho^f \hat{c}_v^f(\theta^f) \big(\frac{\partial \theta^f}{\partial t} + v \frac{\partial \theta^f}{\partial z}\big).
\end{aligned} \tag{3.7}$$

Usually, in FBRs the diffusion term in the previous equation can be neglected against source terms $A^f \boldsymbol{\delta}^f$ and $\mathbf{g}$. Thus, the energy equation (3.2) can be finally written as

$$\begin{aligned}
&\varepsilon^f \rho^f \hat{c}_v^f(\theta^f) \big(\frac{\partial \theta^f}{\partial t} + v \frac{\partial \theta^f}{\partial z}\big) - \frac{1}{r}\frac{\partial}{\partial r}\Big(k_r^f r \frac{\partial \theta^f}{\partial r}\Big) - \frac{\partial}{\partial z}\Big(k_z^f \frac{\partial \theta^f}{\partial z}\Big) \\
&= f - \hat{\mathbf{w}}(\theta^f) \cdot \big(A^f \boldsymbol{\delta}^f(\theta^f, \mathbf{y}^f) + \mathbf{g}\big).
\end{aligned} \tag{3.8}$$

3.1.1 Boundary conditions

For the fluid bulk the boundary conditions are imposed on the boundary of the reactor.

- Reactor entrance ($z = 0$).
  1. Mass:
  $$- D_z^f \frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f)(r, 0, t) + v\varepsilon^f \mathbf{y}^f(r, 0, t) = v\varepsilon^f \mathbf{y}_{in}^f(t), \tag{3.9}$$
  where $\mathbf{y}_{in}^f$ (mol/m^3) is the vector of species concentrations in the bulk fluid entering into the reactor. The right-hand side is the vector of species mass flux (mol/(m^2 s)) (with respect to the entrance surface of the reactor) entering the reactor at time t, at any point $(r, 0)$.
  2. Energy:
  $$\theta^f(r, 0, t) = \theta_{in}^f(t). \tag{3.10}$$
- Reactor exit ($z = L$).
  1. Mass:
  $$\frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f)(r, L, t) = \mathbf{0}. \tag{3.11}$$
  2. Energy:
  $$\frac{\partial \theta^f}{\partial z}(r, L, t) = 0. \tag{3.12}$$
- Reactor walls ($r = R$).
  1. Mass:
  $$\frac{\partial}{\partial r}(\varepsilon^f \mathbf{y}^f)(R, z, t) = \mathbf{0}. \tag{3.13}$$
  2. Energy:
  $$k^f \frac{\partial \theta^f}{\partial r}(R, z, t) = h_{ext}\Big(\theta_{ext}(t) - \theta^f(R, z, t)\Big), \tag{3.14}$$
  where h_{ext} (W/(m^{2}K)) is a heat transfer coefficient between the fluid bulk and the exterior of the reactor and θ_{ext} denotes the temperature of the latter.
- Reactor axis: ($r = 0$).
  1. Mass:
  $$\frac{\partial \varepsilon^f \mathbf{y}^f}{\partial r}(0, z, t) = \mathbf{0}. \tag{3.15}$$
  2. Energy:
  $$\frac{\partial \theta^f}{\partial r}(0, z, t) = 0. \tag{3.16}$$

3.1.2 Initial conditions

1. Mass:
$$\mathbf{y}^f(r,z,0) = \mathbf{y}_0^f(r,z). \tag{3.17}$$
2. Energy:
$$\theta^f(r,z,0) = \theta_0^f(r,z). \tag{3.18}$$

3.2 Modelling the micro-scale

We assume spherical coordinates for the micro-scale. The domain shown in Figure 3.3 is considered:

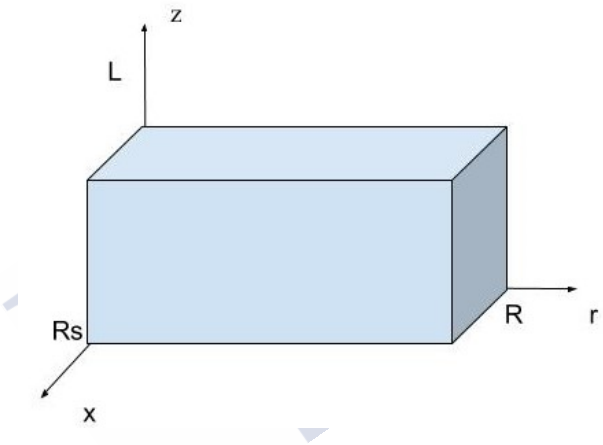

Figure 3.3: Micro-scale domain

We assume that the catalytic solid consists, at the micro-scale level, of porous spherical particles with porosity $\varepsilon^s(r_s,r,z,t)$ (ratio of particle pore volume to particle volume) in which the species diffuse and react. Thus, at each point of the reactor (r,z) there is a particle representative of the porous bed, interacting with the fluid located at this point. Let us write a model for this particular particle. We assume that all fields inside the particle have spherical symmetry which means that they only depend on time and radial variable r_s. Thus, the species mass conservation equations read as follows

$$\frac{\partial \varepsilon^s \mathbf{y}^s}{\partial t} - \frac{1}{r_s^2}\frac{\partial}{\partial r_s}\left(D^s r_s^2 \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial r_s}\right) = A^s \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s), \tag{3.19}$$

where $\mathbf{y}^s(r_s,r,z,t)$ (mol/m^3) denotes the vector of species concentrations in the fluid occupying the intraparticle pores of the particle located at point (r,z) of

the reactor and D^s (m^2/s) is the diagonal matrix containing the mass diffusion coefficients of species in the solid bed.

On the other hand, the energy conservation equation is

$$\frac{\partial(\rho^s \varepsilon^s e^s)}{\partial t} - \frac{1}{r_s^2}\frac{\partial}{\partial r_s}\Big(k^s r_s^2 \frac{\partial \theta^s}{\partial r_s}\Big) = 0. \tag{3.20}$$

Similar to the fluid bulk, we have

$$e^s = \sum_{i=1}^{N} Y_i^s e_i^s,$$

where Y_i^s denotes the mass fraction of species E_i. Since

$$\rho^s Y_i^s = \mathcal{M}_i y_i^s,$$

then

$$\varepsilon^s \rho^s e^s = \varepsilon^s \sum_{i=1}^{N} \rho^s Y_i^s e_i^s = \varepsilon^s \sum_{i=1}^{N} \mathcal{M}_i y_i^s e_i^s$$

and, by using (3.20),

$$\begin{aligned}
&\frac{\partial(\varepsilon^s \rho^s e^s)}{\partial t} = \sum_{i=1}^{N} \mathcal{M}_i \Big(\frac{\partial(\varepsilon^s y_i^s)}{\partial t} e_i^s + \varepsilon^s y_i^s \frac{\partial e_i^s}{\partial t}\Big) \\
&= \sum_{i=1}^{N} \hat{w}_i(\theta^s) \frac{\partial(\varepsilon^s y_i^s)}{\partial t} + \varepsilon^s \sum_{i=1}^{N} \mathcal{M}_i y_i^s \hat{c}_{vi}(\theta^s) \frac{\partial \theta^s}{\partial t} \\
&= \hat{\mathbf{w}}(\theta^s) \cdot \Big[\frac{1}{r_s^2}\frac{\partial}{\partial r_s}\Big(D^s r_s^2 \frac{\partial(\varepsilon^s \mathbf{y}^s)}{\partial r_s}\Big) + A^s \hat{\boldsymbol{\delta}}^s(\theta^s, \mathbf{y}^s)\Big] + \varepsilon^s \rho^s \hat{c}_v^s(\theta^s) \frac{\partial \theta^s}{\partial t}.
\end{aligned} \tag{3.21}$$

In practical cases, the diffusion term in the previous equation can be neglected against the reaction term. Thus, the energy equation (3.20) can be finally written as

$$\varepsilon^s \rho^s \hat{c}_v^s(\theta^s) \frac{\partial \theta^s}{\partial t} - \frac{1}{r_s^2}\frac{\partial}{\partial r_s}\Big(k^s r_s^2 \frac{\partial \theta^s}{\partial r_s}\Big) = -\hat{\mathbf{w}}(\theta^s) \cdot A^s \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s). \tag{3.22}$$

3.2.1 Boundary conditions

Let $d^s(r, z, t)$ be the diameter at time t of the particle located at point (r, z) and $R^s(r, z, t) = d^s(r, z, t)/2$ its radius.

- Center of the particle ($r_s = 0$). Symmetry condition.

  Mass:

$$\frac{\partial \varepsilon^s \mathbf{y}^s}{\partial r_s}(0, r, z, t) = \mathbf{0}. \tag{3.23}$$

  Energy:

$$\frac{\partial \theta^s}{\partial r_s}(0, r, z, t) = 0. \tag{3.24}$$

- Surface of the particle ($r_s = R^s(r, z, t)$). Different possibilities can be considered:

  – Dirichlet condition (no resistance):

  Mass:

$$\mathbf{y}^s(R^s(r, z, t), r, z, t) = \mathbf{y}^f(r, z, t). \tag{3.25}$$

  Energy:

$$\theta^s(R^s(r, z, t), r, z, t) = \theta^f(r, z, t). \tag{3.26}$$

  – Robin boundary conditions (resistance):

  Mass:

$$D^s \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial r_s}(R^s(r, z, t), r, z, t) = \eta_{fs}(r, z, t)\Big(\mathbf{y}^f(r, z, t) - \mathbf{y}^s(R^s(r, z, t), r, z, t)\Big). \tag{3.27}$$

  Energy:

$$k^s \frac{\partial \theta^s}{\partial r_s}(R^s(r, z, t), r, z, t) = h_{fs}(r, z, t)\Big(\theta^f(r, z, t) - \theta^s(R^s(r, z, t), r, z, t)\Big), \tag{3.28}$$

  where η_{fs} and h_{fs} are given coefficients

3.2.2 Initial conditions

1. Mass:

$$\mathbf{y}^s(r_s, r, z, 0) = \mathbf{y}_0^s(r_s, r, z). \tag{3.29}$$

2. Energy:

$$\theta^s(r_s, r, z, 0) = \theta_0^s(r_s, r, z). \tag{3.30}$$

3.3 Sources of mass and energy in the fluid bulk

In order to complete the model, we only need to compute the source terms in the fluid bulk equations, namely, $\mathbf{g}(r,z,t))$ (respectively, $f(r,z,t)$), which is the mass flow rate (respectively, the heat flow rate) per unit of volume provided by the solid particles to the fluid bulk at point (r,z) at time t. For this purpose, we consider

$$D^s \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial r_s}(R^s(r,z,t),r,z,t)$$

which is the species mass flux (i.e., the rate of mass flow rate per unit area, kg/(m^{2}s)) entering the particle across its surface. Similarly,

$$k^s \frac{\partial \theta^s}{\partial r_s}(R^s(r,z,t),r,z,t)$$

is the heat flux (i.e., the rate of heat flow per unit area, J/(m^2 s)) entering the particle across its surface.

Let us denote by $a(r,z,t)$ (m^{-1}) the external surface area of the particles per unit reactor volume at point (r,z) and time t. Since we are assuming spherical particles, we have

$$a(r,z,t) = \frac{4\pi R_s^2}{\frac{4}{3}\pi R_s^3}\big(1-\varepsilon^f(r,z,t)\big) = \frac{3\big(1-\varepsilon^f(r,z,t)\big)}{R_s}. \tag{3.31}$$

Then the mass flow rates of species per unit reactor volume (mol/(m^3 s)) supplied by the particles to the fluid bulk at point (r,z) and time t is given by

$$\mathbf{g}(r,z,t) := -a(r,z,t)D^s \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial r_s}(R^s(r,z,t),r,z,t). \tag{3.32}$$

Moreover, in the case of resistance

$$\mathbf{g}(r,z,t) = a(r,z,t)\eta_{fs}(r,z,t)\Big(\mathbf{y}^s\big(R^s(r,z,t),r,z,t\big) - \mathbf{y}^f(r,z,t)\Big). \tag{3.33}$$

In a similar way, the rate of internal energy per unit reactor volume supplied by the particles to the fluid bulk at point (r,z) and time t is

$$f(r,z,t) = -a(r,z,t)k^s \frac{\partial \theta^s}{\partial r_s}(R^s(r,z,t),r,z,t) + \hat{\mathbf{w}}(\theta)\cdot\mathbf{g}, \tag{3.34}$$

where the first term on the right-hand side represents the flow rate of internal energy per unit reactor volume (W/m^3) from the solid particles to the liquid. In the case of resistance, f becomes

$$f(r,z,t) = a(r,z,t)h_{fs}(r,z,t)\Big(\theta^s\big(R^s(r,z,t),r,z,t\big) - \theta^f(r,z,t)\Big) + \hat{\mathbf{w}}(\theta)\cdot\mathbf{g}. \tag{3.35}$$

The full model of an FBR for the case of resistance can be written as follows:

$$\frac{\partial}{\partial t}(\varepsilon^f \mathbf{y}^f) + \frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f v) - \frac{1}{r}\frac{\partial}{\partial r}\Big(D_r^f r \frac{\partial}{\partial r}(\varepsilon^f \mathbf{y}^f)\Big) - \frac{\partial}{\partial z}\Big(D_z^f \frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f)\Big)$$
$$= A^f \boldsymbol{\delta}^f(\theta^f, \mathbf{y}^f) + a\eta_{fs}\big(\mathbf{y}^s(R^s) - \mathbf{y}^f\big),$$

$$\varepsilon^f \rho^f \hat{c}_v^f(\theta^f)\Big(\frac{\partial \theta^f}{\partial t} + v\frac{\partial \theta^f}{\partial z}\Big) - \frac{1}{r}\frac{\partial}{\partial r}\Big(k_r^f r \frac{\partial \theta^f}{\partial r}\Big) - \frac{\partial}{\partial z}\Big(k_z^f \frac{\partial \theta^f}{\partial z}\Big)$$
$$= a h_{fs}\big(\theta^s(R^s) - \theta^f\big) - \hat{\mathbf{w}}(\theta^f) \cdot A^f \boldsymbol{\delta}^f(\theta^f, \mathbf{y}^f),$$

$$\frac{\partial}{\partial t}(\varepsilon^s \mathbf{y}^s) - \frac{1}{r_s^2}\frac{\partial}{\partial r_s}\Big(D^s r_s^2 \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial r_s}\Big) = A^s \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s),$$

$$\varepsilon^s \rho^s \hat{c}_v^s(\theta^s)\frac{\partial \theta^s}{\partial t} - \frac{1}{r_s^2}\frac{\partial}{\partial r_s}\Big(k^s r_s^2 \frac{\partial \theta^s}{\partial r_s}\Big) = -\hat{\mathbf{w}}(\theta^s) \cdot A^s \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s),$$

$$-D_z^f \frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f)(r, 0, t) + v\varepsilon^f \mathbf{y}^f(r, 0, t) = v\varepsilon^f \mathbf{y}_{in}^f(t),$$

$$\theta^f(r, 0, t) = \theta_{in}^f(t),$$

$$\frac{\partial \varepsilon^f \mathbf{y}^f}{\partial z}(r, L, t) = \mathbf{0},$$

$$\frac{\partial \theta^f}{\partial z}(r, L, t) = 0,$$

$$\frac{\partial \varepsilon^f \mathbf{y}^f}{\partial r}(R, z, t) = \mathbf{0},$$

$$k_r^f \frac{\partial \theta^f}{\partial r}(R, z, t) = h_{ext}\big(\theta_{ext}(t) - \theta^f(R, z, t)\big),$$

$$\frac{\partial \varepsilon^f \mathbf{y}^f}{\partial r}(0, z, t) = \mathbf{0},$$

$$\frac{\partial \theta^f}{\partial r}(0, z, t) = 0,$$

$$\frac{\partial (\varepsilon^s \mathbf{y}^s)}{\partial r_s}(0, r, z, t) = \mathbf{0},$$

$$\frac{\partial \theta^s}{\partial r_s}(0, r, z, t) = 0,$$

$$D^s \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial r_s}(R^s(r, z, t), r, z, t) = \eta_{fs}(r, z, t)\Big(\mathbf{y}^f(r, z, t) - \mathbf{y}^s(R^s(r, z, t), r, z, t)\Big),$$

$$k^s \frac{\partial \theta^s}{\partial r_s}(R^s(r, z, t), r, z, t) = h_{fs}(r, z, t)\big(\theta^f(r, z, t) - \theta^s(R^s(r, z, t), r, z, t)\big),$$

$$\mathbf{y}^f(r, z, 0) = \mathbf{y}_0^f(r, z), \qquad \theta^f(r, z, 0) = \theta_0^f(r, z),$$
$$\mathbf{y}^s(r_s, r, z, 0) = \mathbf{y}_0^s(r_s, r, z), \qquad \theta^s(r_s, r, z, 0) = \theta_0^s(r_s, r, z).$$

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Conclusions

In this part, we have constructed the mathematical model of stirred tank reactors (batch and semi-batch STR and also for continuous STR) and plug flow reactors. We have considered both the transient and the steady-state cases. Reactors are not supposed to be either adiabatic or isotherm, so temperature as well as species concentrations have to be computed by the models that are obtained from the energy and mass conservation equations, respectively.

We have modelled the general $n-$dimensional model which has been particularized to the PFR model. The mathematical model is a coupled system of partial differential equations involving gradient and Laplacian with respect to spatial variables and partial derivative with respect to time.

Finally, we have obtained the model of the FBR which has been understood as a heterogeneous reaction system in which plug-flow is assumed. The model is based on the conservation laws for mass, energy and momentum, and leads to partial differential equations. We have considered the bed as a continuum of small particles (solids spheres) containing the catalyst and interacting with the fluid. Accordingly, spherical symmetry has been assumed. The fluid bulk has been modelled as flowing in a porous media.

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Part II

Mathematical analysis and numerical solution

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Introduction

At the beginning of this part of the thesis we focus on the $n-$dimensional reactor described in Chapter 2. As we have already mentioned, equations in reaction-diffusion systems have been studied by different approaches using a variety of methods.

The objective here is to prove global existence of solution for convection-diffusion-reaction systems. The topic is classical and studied along time. Even if the analysis on this problem has been done over two centuries, no comprehensive mathematical theory has been established, on the contrary, the literature is full of challenging open problems. In several space dimensions, not even the global existence of solutions is presently known in any significant degree of generality. Until now, most of the analysis has been concerned with the one-dimensional case.

The proof of the global theorem is based on the techniques in [55]. In this article, the local existence of the reaction–diffusion systems is provided via the semigroup theory by considering the semilinear parabolic problem. However, we combine this theory with the variational approach. In that case we have to sacrifice regularity of the solution. Of course, this solution is understood in the weak sense. Going back to the global solution, properties **(P)** and **(M)**, that will hold because of the form of our particular reaction term (the law of mass action), play an important role in the existence proof. The variables in our problem represent species concentration so, their positivity is a natural property (helpful to verify **(P)**).

Control and optimization problems in chemical engineering and their applications often require many numerical simulations of large-scale dynamical systems with different conditions. If a fast or real-time control strategy is desired, the direct numerical simulation does not work well. It is important to know how the error behaves. In Chapter 5 an error estimation is obtained by following the techniques in [63]. The proposed approach approximates the nonlinear function by its Lagrange interpolant. To make sure that we can do these estimations we need previously to prove the existence of solution of the semidiscretized problem we use in the estimations. Once this study has been

carried out, it is necessary to compute a numerical solution of the model that interests us from the practical point of view. We focus on PFR and FBR models. For the first one we use a finite difference scheme and for the second one the finite element method is applied.

Chapter 4

Existence and uniqueness of solution in convection-diffusion-reaction systems

The study of existence and uniqueness of solution in convection-diffusion-reaction systems is an interesting topic which represents a challenging task due to the non-linearity of the source term, the coupling of the equations and, sometimes, even the existence of non-linear diffusion terms. During the last decades, this problem was treated from different points of view. Some authors studied only the local existence. Others treated the problem through weak formulation and some of them worked with classical solutions and particular assumptions on the source term and/or the initial conditions. Different boundary conditions can be considered. The existing results in the literature are focused on two-dimensional models, but in many situations extension to more general $n-$dimensional case can be done.

Some authors use approaches that involve Lyapunov functions, but the use of semigroup theory still has a great impact in this research field. Other interesting approaches use the concepts of upper and lower solutions, or the positivity of the solution and the control of mass. These techniques are briefly described in the following paragraphs.

In the paper of Amman [1] a semilinear parabolic system is considered and interpreted as an abstract evolution system. A theory of existence, regularity

and continuous dependence is developed, but only local existence is proved.

The global existence for the two-dimensional model was first demonstrated in [35] using semigroup theory and the n-dimensional model with convection-diffusion terms was studied in [60]. Two important references for this approach are [40] and [54].

The technique of upper and lower solution is developed by Pao in [53] for coupled parabolic systems with Robin conditions.

The case of coupled or cross-diffusion terms is treated in the thesis [15]. In addition, for two-dimensional models, a technique that employs the sign function is used to prove existence of a classical solution, see for example [16].

Lyapunov functions are used in [25] to prove existence of weak solutions global in time for more general diffusion terms. Lyapunov structure is also applied to a general class of Lotka-Volterra systems in [28] or with L^p-bounds, $p \geq 1$ [38]. The one-dimensional case with convection-diffusion terms and Dirichlet boundary conditions is studied in [50] via Lyapunov type conditions. A general domain is considered in [48] and [49] for existence and boundedness of global solution of a diffusion-reaction problem.

Global existence in time of solutions for reaction-diffusion systems relies on two essential properties: positivity of solution along time and boundedness of total mass in [61]. These properties are also used in [55] and [39], where weak and strong formulations of the problem are described, and some representative examples are given. Similar methodology for polynomial growth of source term is presented in [45] for two-dimensional systems. Besides, L^p, $p \geq 1$, and L^∞-approaches also appear in these references. L^∞-blow up may occur in reaction-diffusion systems even if they seem simple. To avoid it, strong assumptions on the source term are required. For more details see, for example, [56]. Let us end this introduction by reproducing the abstract of the interesting survey by M. Pierre [55]:

The goal of this paper is to describe the state of the art on the question of global existence of solutions to reaction-diffusion systems for which two main properties hold: on the one hand, the positivity of the solutions is preserved for all time; on the other hand, the total mass of the components is uniformly controlled in time. This uniform control on the mass (or –in mathematical terms– on the L^1-norm of the solution) suggests that no blow up should occur in finite time. It turns out that the situation is not so simple. This explains why so many partial results in different directions are found in the literature on this

topic, and why also the general question of global existence is still open, while lots of systems arise in applications with these two natural properties.

Throughout this chapter we will prove global existence of solution for some convection-diffusion-reaction systems. The proof of such theorem is based on some properties described in [55] but, first, the techniques we employ are slightly different (they combine semigroup theory and weak formulation techniques) and, second, we include a convection term which is mandatory to model most of industrial chemical reactors. The properties mentioned in the previous paragraph will be verified for our particular reaction term which corresponds to the law of mass action. The variables in our problem represent species concentration, so their positivity is a natural property. Firstly, we will prove local existence of solution by using semigroup theory and then we will prove that it is bounded in L^∞, which will allow us to conclude the existence of a global solution. For the document to be self-contained we detail the proofs of all the results, although some of them have been previously obtained or use techniques that are standard in the mathematical analysis of partial differential equations.

4.1 The model

We focus on $n-$dimensional convection-diffusion-reaction models for chemical reactors. The mathematical modelling of these reactors was described in detail in Chapter 2. In this chapter we only consider the system related to chemical species, so we assume that temperature is known. We adopt this simplification because the property of boundedness of total mass needed for the global existence cannot be shown for the energy equation.

Let us recall and establish the assumptions we consider:

- Robin boundary conditions at the entrance of the reactor.
- Homogeneous Neumann boundary condition at the exit of the reactor.
- Null mass flux through the wall of the reactor.
- The reaction term is given by the law of mass action and the Arrhenius law.
- The diffusion coefficients are all equal to $d > 0$.

Remark 4.1.1. *Considering equal diffusion coefficients is not an innocent assumption as it has been noticed in [55].*

Summarizing, in the present chapter, the following convection-diffusion-reaction system will be studied:

$$(P)\begin{cases} \dfrac{\partial \mathbf{y}}{\partial t}(t,x) + \nabla \mathbf{y}(t,x)\mathbf{v} - d\Delta \mathbf{y}(t,x) = \boldsymbol{\varphi}(t,x,\mathbf{y}(t,x)), & (t,x) \in (0,T)\times\Omega, \\ \mathbf{y}(0,x) = \mathbf{y}_0(x), \ x \in \Omega, \\ d\dfrac{\partial \mathbf{y}}{\partial \boldsymbol{\nu}}(t,x) - (\mathbf{v}(x)\cdot\boldsymbol{\nu}(x))\mathbf{y}(t,x) = \mathbf{g}(t,x), & (t,x) \in (0,T)\times\Gamma_1, \\ d\dfrac{\partial \mathbf{y}}{\partial \boldsymbol{\nu}}(t,x) = \mathbf{0}, & (t,x) \in (0,T)\times(\Gamma_2\cup\Gamma_3), \end{cases}$$

where Ω is a bounded domain in $\mathbb{R}^n$ with smooth boundary $\partial\Omega$, as represented in Figure 2.1 and ν is the outward unit normal vector to $\partial\Omega$. Recall that Γ_1 denotes the reactor entrance, Γ_2 the reactor exit and Γ_3 the reactor wall. We recall that $\mathbf{y}(t,x) \in \mathbb{R}^N$, N being the number of species. Moreover, for now we assume that

$$\boldsymbol{\varphi} : (t,x,\mathbf{w}) \in (0,T)\times\Omega\times\mathbb{R}^N \to \boldsymbol{\varphi}(t,x,\mathbf{w}) \in \mathbb{R}^N$$

is a Carathéodory function, i.e., it is measurable with respect to (t,x) and continuous with respect to $\mathbf{w}$.

Let us recall that if $\boldsymbol{\varphi}$ corresponds to the law of mass action with the Arrhenius law, it can be written as

$$\boldsymbol{\varphi}(t,x,\mathbf{w}) = A\boldsymbol{\delta}(t,x,\mathbf{w}), \quad (t,x,\mathbf{w}) \in [0,T]\times\Omega\times\mathbb{R}^N,$$

with $\boldsymbol{\delta}$ given by (1.4) and (1.5) with non-negative integer exponents α_i^l, $i = 1,\dots,N$, $l = 1,\dots L$, which represent the coefficients of the $i-$th reactant in the $l-$th reaction.

4.2 Local existence of weak solution

In this section we study the existence and uniqueness of solution of problem (P) in an open interval $(0,\delta)$, for some $\delta > 0$. This local solution is intended in a "weak sense" via the variational formulation of the problem that is given below. In what follows τ denotes a positive real number and $\langle .,. \rangle$ the duality between spaces $(\mathbf{H}^1(\Omega))'$ and $\mathbf{H}^1(\Omega))$.

Let us define the bilinear continuous form $a : \mathbf{H}^1(\Omega)\times\mathbf{H}^1(\Omega) \to \mathbb{R}$ by

$$a(\mathbf{y},\mathbf{w}) := \int_\Omega \nabla\mathbf{y}(x)\mathbf{v}(x)\cdot\mathbf{w}(x) + \int_\Omega d\nabla\mathbf{y}(x) : \nabla\mathbf{w}(x) - \int_{\Gamma_1} (\mathbf{v}(x)\cdot\boldsymbol{\nu}(x))\mathbf{y}(x)\cdot\mathbf{w}(x) \tag{4.1}$$

and the linear continuous form $l(t) : \mathbf{H}^1(\Omega) \to \mathbb{R}$ by

$$l(t)(\mathbf{w}) := \int_{\Gamma_1} \mathbf{g}(t,x) \cdot \mathbf{w}(x). \tag{4.2}$$

Definition 4.2.1. *Let* $\mathbf{v} \in \mathbf{L}^\infty(\Omega)$ *with* $\operatorname{div} \mathbf{v} = 0$ *and* $\mathbf{v} \cdot \boldsymbol{\nu} \in L^\infty(\Gamma_1)$, $\mathbf{g} \in \mathbf{L}^2(0,\tau;\mathbf{L}^2(\Gamma_1))$ *and* $\mathbf{y}_0 \in \mathbf{L}^2(\Omega)$. *A function* $\mathbf{y} \in L^2((0,\tau);\mathbf{H}^1(\Omega))$*such that* $\dfrac{\partial \mathbf{y}}{\partial t} \in \mathbf{L}^2(0,\tau;(\mathbf{H}^1(\Omega))')$ *and* $\boldsymbol{\varphi}(t,x,\mathbf{y}(t,x)) \in L^2(0,T;\mathbf{L}^2(\Omega))$ *is said a* ***weak solution*** *of problem* (4.3)-(4.4) *if and only if*

$$\langle \frac{\partial \mathbf{y}}{\partial t}(t), \mathbf{w} \rangle + a(\mathbf{y}(t), \mathbf{w}) = \int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{y}(t,x)) \cdot \mathbf{w}(x) + l(t)(\mathbf{w}) \ \forall \mathbf{w} \in \mathbf{H}^1(\Omega), \tag{4.3}$$

$$\mathbf{y}(0) = \mathbf{y}_0. \tag{4.4}$$

We work with a first order in time semi-linear parabolic partial differential equation (PDE) system. A first attempt to prove a local existence result for our system would consists in building an adequate contraction in order to use the Banach fixed point theorem (it is described in [3], also known in [36] as the Banach Contraction Principle). Unfortunately, we are not able to prove the Lipschitz property in the Banach space where the mapping is defined.

This is why we use the semigroup theory where the local existence theory for a first order in time parabolic PDE system is seen as an extension of the ODEs theory. In this framework some hypotheses such as Hölder condition and locally Lipschitz property of the reaction term are needed. One of the difficulties when applying semigroup theory is that only homogeneous boundary conditions are allowed (in our case $\mathbf{g}$ should be null). Thus, we proceed in two steps to build the solution of the non-homogeneous problem. Firstly, a translation is introduced to get homogeneous boundary condition and then semigroup theory is applied. Finally, the two steps provides us with a unique continuous solution.

4.2.1 Existence of solution to an auxiliary elliptic problem

In order to make a translation in the weak problem (4.3)–(4.4), we introduce a family of *linear* elliptic problems with Robin boundary condition $\mathbf{g}$ at the

entrance Γ_1, parametrized by the time variable t, namely,

$$(P_G)\begin{cases}\nabla\mathbf{G}(t,x)\mathbf{v}(x) - d\Delta\mathbf{G}(t,x) = \mathbf{0}, & (t,x)\in(0,T)\times\Omega,\\ d\dfrac{\partial\mathbf{G}}{\partial\boldsymbol{\nu}}(t,x) - (\mathbf{v}(x)\cdot\boldsymbol{\nu}(x))\mathbf{G}(t,x) = \mathbf{g}(t,x), & (t,x)\in(0,T)\times\Gamma_1,\\ d\dfrac{\partial\mathbf{G}}{\partial\boldsymbol{\nu}}(t,x) = \mathbf{0}, & (t,x)\in(0,T)\times(\Gamma_2\cup\Gamma_3),\end{cases}$$

and its weak formulation: find $\mathbf{G}(t)\in\mathbf{H}^1(\Omega)$ such that

$$a(\mathbf{G}(t),\mathbf{w}) = l(t)(\mathbf{w}) \text{ for } \mathbf{w}\in\mathbf{H}^1(\Omega). \tag{4.5}$$

We notice that time t is a parameter rather than an independent variable because there are no time derivatives in (4.5). Now, let us prove that, under some assumptions, this problem has a unique weak solution that is also continuous.

Proposition 4.2.1. *Let $n\geq 2$. Under the assumptions,*

- $\mathbf{v}\in\mathbf{L}^\infty(\Omega)$,
- $\mathrm{div}\mathbf{v} = 0$,
- $\mathbf{v}\cdot\boldsymbol{\nu}\in L^\infty(\partial\Omega)$,
- $\mathbf{v}\cdot\boldsymbol{\nu}\leq 0$ *on* Γ_1, $\mathbf{v}\cdot\boldsymbol{\nu}\geq 0$ *on* Γ_2, $\mathbf{v}\cdot\boldsymbol{\nu} = 0$ *on* Γ_3,
- *there exists* $S\subset\Gamma_2$ *with non null surface measure and* $\alpha>0$ *such that* $\mathbf{v}\cdot\boldsymbol{\nu}\geq\alpha$ *on* S,
- $\mathbf{g}\in\mathbf{W}^{1,1}(0,T;\mathbf{L}^p(\Gamma_1))$ *with* $p = n-1+\varepsilon$ *for* $n>2$ *or* $\mathbf{g}\in\mathbf{W}^{1,1}(0,T;\mathbf{L}^2(\Gamma_1))$ *for* $n=2$.

Then, problem (4.5) has a unique solution $\mathbf{G}\in\mathbf{W}^{1,1}(0,T;\mathbf{H}^1(\Omega)\cap\boldsymbol{\mathcal{C}}^{0,\gamma}(\Omega))$ *where* γ *is a suitable number,* $\gamma\in(0,1)$*, and hence, in particular,* $\mathbf{G}\in\boldsymbol{\mathcal{C}}([0,T]\times\overline{\Omega})$.

Proof.

Firstly, for $t\in[0,\tau]$ the Lax-Milgram lemma provides us a unique solution $\mathbf{G}(t,.)\in\mathbf{H}^1(\Omega)$. Indeed, we have

1) *l(t) is linear continuous in* $\mathbf{H}^1(\Omega)$:

$$|l(t)(\mathbf{w})| = \Big|\int_{\Gamma_1}\mathbf{g}(t)\cdot\mathbf{w}\Big| \leq \int_{\Gamma_1}|\mathbf{g}(t)\cdot\mathbf{w}|.$$

By applying Hölder inequality we have

$$|l(t)(\mathbf{w})| \leq \|\mathbf{g}(t)\|_{\mathbf{L}^p(\Gamma_1)}\|\mathbf{w}\|_{\mathbf{L}^q(\Gamma_1)},$$

where $\frac{1}{p}+\frac{1}{q}=1$. For $n>2$ we take $p=n-1+\varepsilon>2$ and then $q<2$. If $n=2$ and $\mathbf{g}\in \mathbf{W}^{1,1}(0,\tau;\mathbf{L}^2(\Gamma_1))$, then $q=2$.

Finally, by using a trace theorem (see, for instance, [51, Theor. 1.2]), we have

$$|l(t)(\mathbf{w})|\leq C\|\mathbf{g}(t)\|_{\mathbf{L}^p(\Gamma_1)}\|\mathbf{w}\|_{\mathbf{H}^1(\Omega)}.$$

2) *a is bilinear continuous in* $\mathbf{H}^1(\Omega)\times\mathbf{H}^1(\Omega)$:

$$\begin{aligned}|a(\mathbf{G},\mathbf{w})| &= \Big|\int_\Omega \nabla\mathbf{G}\mathbf{v}\cdot\mathbf{w}+\int_\Omega d\nabla\mathbf{G}:\nabla\mathbf{w}-\int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})\mathbf{G}\cdot\mathbf{w}\Big|\\ &\leq \Big|\int_\Omega \nabla\mathbf{G}\mathbf{v}\cdot\mathbf{w}\Big|+\Big|\int_\Omega d\nabla\mathbf{G}:\nabla\mathbf{w}\Big|+\Big|\int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})\mathbf{G}\cdot\mathbf{w}\Big|\\ &\leq \int_\Omega|\nabla\mathbf{G}\mathbf{v}\cdot\mathbf{w}|+d\int_\Omega|\nabla\mathbf{G}:\nabla\mathbf{w}|+\int_{\Gamma_1}|(\mathbf{v}\cdot\boldsymbol{\nu})\mathbf{G}\cdot\mathbf{w}|.\end{aligned}$$

By using Hölder's inequality we obtain,

$$\begin{aligned}&|a(\mathbf{G},\mathbf{w})|\leq\left(\int_\Omega\|\nabla\mathbf{G}\|^2\|\mathbf{v}\|^2\right)^{\frac12}\|\mathbf{w}\|_{\mathbf{L}^2(\Omega)}+d\|\nabla\mathbf{G}\|_{\mathbf{L}^2(\Omega)}\|\nabla\mathbf{w}\|_{\mathbf{L}^2(\Omega)}\\ &+\|\mathbf{v}\cdot\boldsymbol{\nu}\|_{\mathbf{L}^\infty(\Gamma_1)}\int_{\Gamma_1}|\mathbf{G}\cdot\mathbf{w}|\end{aligned}$$

and by applying Hölder's inequality we get, for $\|\mathbf{v}\|_{\mathbf{L}^\infty(\Omega)}:=\||\mathbf{v}|\|_{L^\infty(\Omega)}$,

$$\begin{aligned}&|a(\mathbf{G},\mathbf{w})|\leq\|\mathbf{v}\|_{\mathbf{L}^\infty(\Omega)}\|\nabla\mathbf{G}\|_{\mathbf{L}^2(\Omega)}\|\mathbf{w}\|_{\mathbf{L}^2(\Omega)}+d\|\nabla\mathbf{G}\|_{\mathbf{L}^2(\Omega)}\|\nabla\mathbf{w}\|_{\mathbf{L}^2(\Omega)}\\ &+\|\mathbf{v}\cdot\boldsymbol{\nu}\|_{\mathbf{L}^\infty(\Gamma_1)}\int_{\partial\Omega}|\mathbf{G}\cdot\mathbf{w}|\\ &\leq\sqrt{2}\max\{\|\mathbf{v}\|_{\mathbf{L}^\infty(\Omega)},d\}\|\nabla\mathbf{G}\|_{\mathbf{L}^2(\Omega)}\|\mathbf{w}\|_{\mathbf{H}^1(\Omega)}\\ &+\|\mathbf{v}\cdot\boldsymbol{\nu}\|_{\mathbf{L}^\infty(\Gamma_1)}\|\mathbf{G}\|_{\mathbf{L}^2(\partial\Omega)}\|\mathbf{w}\|_{\mathbf{L}^2(\partial\Omega)}.\end{aligned}$$

Finally, by using again the trace theorem in [51], we conclude that

$$\begin{aligned}&|a(\mathbf{G},\mathbf{w})|\leq C(\mathbf{v})\|\mathbf{G}\|_{\mathbf{H}^1(\Omega)}\|\mathbf{w}\|_{\mathbf{H}^1(\Omega)},\\ &\mathbf{w}\in\mathbf{H}^1(\Omega).\end{aligned}$$

3) *a is coercive*

Indeed, firstly,

$$a(\mathbf{G},\mathbf{G})=\int_\Omega\nabla\mathbf{G}\mathbf{v}\cdot\mathbf{G}+\int_\Omega d\nabla\mathbf{G}:\nabla\mathbf{G}-\int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{G}\|^2.$$

Moreover, we have

$$\nabla \mathbf{G}\mathbf{v}\cdot\mathbf{G} = \mathbf{v}\cdot(\nabla\mathbf{G})^T\mathbf{G} = \frac{1}{2}\mathbf{v}\cdot\nabla(\mathbf{G}\cdot\mathbf{G}) = \frac{1}{2}\mathbf{v}\cdot\nabla(\|\mathbf{G}\|^2).$$

Then, using that div$\mathbf{v}=0$ we have

$$\begin{aligned} a(\mathbf{G},\mathbf{G}) &= \frac{1}{2}\int_{\partial\Omega}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{G}\|^2 + \int_\Omega d\nabla\mathbf{G}:\nabla\mathbf{G} - \int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{G}\|^2 \\ &= \frac{1}{2}\int_{\Gamma_2}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{G}\|^2 + \int_\Omega d\|\nabla\mathbf{G}\|^2 - \frac{1}{2}\int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{G}\|^2. \end{aligned}$$

Notice that, on the inlet boundary Γ_1, $\mathbf{v}\cdot\boldsymbol{\nu}\le 0$ and on subset S of the outlet boundary Γ_2, $\mathbf{v}\cdot\boldsymbol{\nu}\ge\alpha$. Hence,

$$\begin{aligned} a(\mathbf{G},\mathbf{G}) &= \frac{1}{2}\int_{\partial\Omega}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{G}\|^2 + \int_\Omega d\|\nabla\mathbf{G}\|^2 - \int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{G}\|^2 \\ &\ge \frac{1}{2}\int_{\Gamma_2}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{G}\|^2 + \int_\Omega d\|\nabla\mathbf{G}\|^2 \ge \frac{\alpha}{2}\int_S\|\mathbf{G}\|^2 + \int_\Omega d\|\nabla\mathbf{G}\|^2 \\ &\ge \beta\|\mathbf{G}\|^2_{\mathbf{H}^1(\Omega)}, \end{aligned}$$

where the last inequality is a consequence of Friedrichs inequality (see, for instance, [51, Theor. 1.1.9]).

Now, by the Lax-Milgram lemma (see, for instance, [27, Lemma 2.2]), there exists a unique $\mathbf{G}(t,.)\in\mathbf{H^1(\Omega)}$ satisfying $a(\mathbf{G}(t),\mathbf{w}) = l(t)(\mathbf{w})\ \ \forall\mathbf{w}\in\mathbf{H^1(\Omega)}$. After that, we obtain the claimed additional regularity by using Theorem 3.14 in [52]. Notice that the hypothesis of $\mathbf{g}\in\mathbf{W}^{1,1}(0,\tau;\mathbf{L}^p(\Gamma_1))$ with $p=n-1+\varepsilon$, which is included in Theorem 3.14., is also satisfied if $n=2$ because we have $\mathbf{g}\in\mathbf{W}^{1,1}(0,\tau;\mathbf{L}^2(\Gamma_1))\subset\mathbf{W}^{1,1}(0,\tau;\mathbf{L}^{1+\varepsilon}(\Gamma_1))$. Finally, this result has been proved for scalar PDEs, but it does not matter because our vector boundary-value problem is fully decoupled into scalar ones:

$$(P_G)_i\begin{cases} \mathbf{v}\cdot\nabla G_i(t,x) - d\Delta G_i(t,x) = 0, & (t,x)\in(0,\tau)\times\Omega, \\ d\dfrac{\partial G_i}{\partial\boldsymbol{\nu}}(t,x) - (\mathbf{v}\cdot\boldsymbol{\nu})G_i(t,x) = g_i(t,x), & (t,x)\in(0,\tau)\times\Gamma_1, \\ d\dfrac{\partial G_i}{\partial\boldsymbol{\nu}}(t,x) = 0, & (t,x)\in(0,\tau)\times\Gamma_2\cup\Gamma_3. \end{cases}$$

Thus, $\mathbf{G}(t,.)\in\boldsymbol{\mathcal{C}}^{0,\gamma}(\Omega)$ for some $\gamma>0$ and fulfills the following inequality:

$$\|\mathbf{G}(\mathbf{t})\|_{\boldsymbol{\mathcal{C}}(\overline{\Omega})} \le \|\mathbf{G}(\mathbf{t})\|_{\boldsymbol{\mathcal{C}}^{0,\gamma}(\Omega)} \le C\|\mathbf{g}(t)\|_{\mathbf{L}^{n-1+\varepsilon}(\Gamma_1)}. \tag{4.6}$$

By integrating in time we deduce that $\mathbf{G} \in \mathbf{L}^1(0,\tau;\boldsymbol{\mathcal{C}}(\overline{\Omega}))$.

Now, let us denote by T the bounded linear operator (from $\mathbf{L}^p(\Gamma_1)$ in $\mathbf{H^1(\Omega)}$) mapping $\mathbf{g} \in \mathbf{L}^p(\Gamma_1)$ into the solution of problem (P_G), $\mathbf{G} \in \mathbf{H}^1(\Omega) \cap \boldsymbol{\mathcal{C}}(\overline{\Omega})$. Since $1 < p < \infty$ then $\mathbf{L}^p(\Gamma_1)$ is a reflexive Banach space and we have (see [20, Cor. A2]),

$$\mathbf{g}(t) = \mathbf{g}(0) + \int_0^t \frac{d\mathbf{g}}{ds}(s)ds.$$

Hence,

$$\mathbf{G}(t) = T\mathbf{g}(t) = T\mathbf{g}(0) + \int_0^t T\frac{d\mathbf{g}}{ds}(s)ds = G(0) + \int_0^t T\frac{d\mathbf{g}}{ds}(s)ds$$

which implies

$$\frac{d\mathbf{G}}{dt}(t) = T\frac{d\mathbf{g}}{dt}(t) \in \mathbf{H}^1(\Omega) \cap \boldsymbol{\mathcal{C}}(\overline{\Omega}).$$

Therefore,

$$\left\| \frac{d\mathbf{G}}{dt}(t) \right\|_{\boldsymbol{\mathcal{C}}(\overline{\Omega})} \leq C \left\| \frac{d\mathbf{g}}{dt}(t) \right\|_{\mathbf{L}^{n-1+\varepsilon}(\Gamma_1)} \tag{4.7}$$

and then $\dfrac{\partial \mathbf{G}}{\partial t} \in \mathbf{L}^1(0,\tau;\boldsymbol{\mathcal{C}}(\overline{\Omega}))$. Finally, from [41, Lemma 1.2.], we deduce that $\mathbf{G} \in \mathcal{C}([0,\tau];\boldsymbol{\mathcal{C}}(\overline{\Omega})) = \boldsymbol{\mathcal{C}}([0,\tau] \times \overline{\Omega})$.

■

4.2.2 Local existence of a homogeneous problem

In this section, in order to get a local solution to problem (4.3)-(4.4) of the form $\mathbf{y} = \mathbf{u} + \mathbf{G}$ we apply the semigroup theory to the following auxiliary nonlinear homogeneous parabolic problem:

$$(P_u) \begin{cases} \dfrac{\partial \mathbf{u}}{\partial t}(t,x) + \nabla \mathbf{u}(t,x)\mathbf{v}(x) - d\Delta \mathbf{u}(t,x) = \hat{\boldsymbol{\varphi}}(t,x,\mathbf{u}(t,x)), \quad (t,x) \in (0,\tau) \times \Omega, \\ d\dfrac{\partial \mathbf{u}}{\partial \boldsymbol{\nu}}(t,x) - (\mathbf{v} \cdot \boldsymbol{\nu})\mathbf{u}(t,x) = \mathbf{0}, \quad (t,x) \in (0,\tau) \times \Gamma_1, \\ d\dfrac{\partial \mathbf{u}}{\partial \boldsymbol{\nu}}(t,x) = \mathbf{0}, \quad (t,x) \in (0,\tau) \times \Gamma_2 \cup \Gamma_3, \\ \mathbf{u}(0,x) = \mathbf{u}_0(x), \ x \in \Omega, \end{cases}$$

where $\hat{\boldsymbol{\varphi}} : [0,T] \times \Omega \times \mathbb{R}^N \to \mathbb{R}^N$ is defined a.e. in $(0,T) \times \Omega \times \mathbb{R}^N$ by

$$\hat{\boldsymbol{\varphi}}(t,x,\mathbf{u}) = \boldsymbol{\varphi}\left(t,x,\mathbf{u} + \mathbf{G}(t,x)\right) - \frac{\partial \mathbf{G}}{\partial t}(t,x) \tag{4.8}$$

and $\mathbf{u}_0(x) := \mathbf{y}_0(x) - \mathbf{G}(0,x)$. We notice that $\hat{\boldsymbol{\varphi}}$ is also a Carathéodory function. Now, in order to apply the semigroup theory, we rewrite problem (P_u) in terms of a second order strongly elliptic operator, to be called $\mathcal{A}$, and a differential operator of order one acting on the boundary, to be called $\mathcal{B}$.

The operator $\mathcal{A}$ contains the diffusion and convection terms in the system described above and it is defined by components in the following way:

$$\mathcal{A}_i(x,D) = d\sum_{k=1}^{n} D_{kk} - \sum_{k=1}^{n} v_k(x) D_k \quad \forall i = 1,...,N \text{ and } x \in \overline{\Omega}, \tag{4.9}$$

where $D_k = \partial/\partial x_k$ and $D_{kk} = \partial^2/\partial x_k^2$. The differential operator $\mathcal{B}$ is defined also by components by

$$\mathcal{B}_j(x,D) = b_0(x)I + \sum_{k=1}^{n} b_{1k}(x) D_k \quad \forall j = 1,...,N \text{ and } x \in \partial\Omega \tag{4.10}$$

with

$$b_0(x) = \begin{cases} -\mathbf{v}(x)\cdot\boldsymbol{\nu}(x), & x \in \Gamma_1 \cup \Gamma_3, \\ 0, & x \in \Gamma_2, \end{cases} \tag{4.11}$$

$$b_{1k}(x) = d\nu_k, \quad k = 1,...,n \text{ and } x \in \partial\Omega. \tag{4.12}$$

Notice that boundary conditions were considered of Robin type in Γ_1 and of Neumann type in $\Gamma_2 \cup \Gamma_3$. However, we can rewrite them as a Robin condition in all the boundary using coefficients b_0 and $\mathbf{b}_1$, where

$$\mathbf{b}_1 = (b_{11}, \ldots, b_{1n})^T.$$

Now problem (P_u) is written as follows

$$(P_u) \begin{cases} \dfrac{\partial u_i}{\partial t}(t,x) = \mathcal{A}_i(x,D)u_i(t,x) + \hat{\varphi}_i(t,x,\mathbf{u}(t,x)), \ (t,x) \in (0,\tau)\times\Omega, \\ \mathcal{B}_i(x,D)u_i(t,x) = 0, \ t \in (0,\tau), \ x \in \partial\Omega, \\ u_i(0,x) = u_{0_i}(x), \ x \in \Omega, \\ \forall i = 1,...,N. \end{cases}$$

In order to use the abstract theory in the following paragraphs, we notice that problem (P_u) can be seen as a semilinear parabolic problem, as the nonlinearity depends on the unknown vector $\mathbf{u}$, but not on its derivatives.

Let $\mathbf{X} := \boldsymbol{\mathcal{C}}(\overline{\Omega};\mathbb{R}^N)$ be endowed with the norm

$$\|\mathbf{u}\|_{\mathbf{X}} := \max_{x\in\overline{\Omega}} \|\mathbf{u}(x)\|_{\mathbb{R}^N},$$

where $\|.\|_{\mathbb{R}^N}$ is a suitable norm in $\mathbb{R}^N$. Since all norms are equivalent we will drop the subscript $\mathbb{R}^N$. Similarly, if there is no ambiguity we will suppress the subscript $\mathbf{X}$ in the above norm in the normed space $\mathbf{X}$.

Let the nonlinear mapping $\hat{\mathbf{f}} : [0,T]\times\mathbf{X}\to\mathbf{X}$ be defined by

$$\hat{\mathbf{f}}(t,\mathbf{u})(x) := \hat{\boldsymbol{\varphi}}(t,x,\mathbf{u}(x)) \ \forall x\in\overline{\Omega}. \tag{4.13}$$

We introduce the linear unbounded operator $\mathbf{A} : D(\mathbf{A})\subset\mathbf{X}\to\mathbf{X}$ to be called ***the realization of*** $\mathcal{A}(\cdot,D)$ in $\mathbf{X}$ as

$$\mathbf{A}\mathbf{u} := \mathcal{A}(\cdot,D)\mathbf{u} \ \ \forall \mathbf{u}\in D(\mathbf{A}),$$

where the domain $D(\mathbf{A})$ is given by

$$D(\mathbf{A}) = \{\mathbf{u}\in \bigcap_{1\le p<\infty} \mathbf{W}^{2,p}(\Omega) : (\mathcal{A}_1u_1,...,\mathcal{A}_Nu_N)^T\in\mathbf{X}, \\ (\mathcal{B}_1u_1,...,\mathcal{B}_Nu_N)^T|_{\partial\Omega} = \mathbf{0}\}. \tag{4.14}$$

Remark 4.2.1. *Homogeneous boundary conditions are needed because $D(\mathbf{A})$ must be a vector space in order to apply semigroup theory. This is why we have introduced vector function $\mathbf{G}$ in order to make a translation.*

We notice that for $p > \dfrac{n}{2}$, the Sobolev embedding theorem (see, for instance, [51, Theorem 3.8, Chap. 2]) implies $\mathbf{W}^{2,p}(\Omega)\subset\boldsymbol{\mathcal{C}}(\overline{\Omega})$. Therefore, $D(\mathbf{A})\subset\boldsymbol{\mathcal{C}}(\overline{\Omega})$ in any spatial dimension.

Now, let us introduce the problem

$$(P_u)\begin{cases} \dfrac{d\mathbf{u}}{dt} = \mathbf{A}\mathbf{u} + \hat{\mathbf{f}}(t,\mathbf{u}), \quad t>0, \\ \mathbf{u}(0) = \mathbf{u}_0. \end{cases} \tag{4.15}$$

In the next paragraphs, we describe some hypotheses for operators $\mathcal{A}$ and $\mathcal{B}$ and mapping $\hat{\boldsymbol{\varphi}}$. These hypotheses must be fulfilled in order to prove a local existence theorem for problem (P_u) by applying the theorems described in Appendix B.

Hypothesis on the domain Ω

(D1) The domain Ω is a bounded open set with $\mathcal{C}^2$ boundary $\partial\Omega$.

Hypotheses on the elliptic differential operator $\mathcal{A}$

(A1) *The diffusion coefficient d is positive.*

(A2) $\mathbf{v} \in \boldsymbol{\mathcal{C}^1}(\overline{\Omega})$.

These assumptions imply the hypotheses for the operator $\mathcal{A}$ that are needed in Appendix B.

Hypotheses on the differential operator $\mathcal{B}$

We can prove all hypotheses regarding the boundary operator $\mathcal{B}$ in Appendix B without any additional assumption. Indeed,

(B1) $b_0 \in \mathcal{C}^1(\overline{\Omega})$
Firstly, we have $b_0 = -\mathbf{v} \cdot \boldsymbol{\nu} \in \mathcal{C}^1(\partial\Omega)$ because both $\mathbf{v}$ and $\boldsymbol{\nu}$ belong to this space and, since $\mathbf{v}(x) \cdot \boldsymbol{\nu}(x) = 0$ for $x \in \Gamma_3$, we can replace $\mathbf{v}(x) \cdot \boldsymbol{\nu}(x)$ by 0 on Γ_2 while preserving the membership to $\mathcal{C}^1(\partial\Omega)$. Finally, b_0 can be extended to the whole domain Ω in such a way that the resulting function belongs to $\mathcal{C}^1(\overline{\Omega})$ by using a result from Ladyzenskaya et al. [40, page 10]. Thus, $b_0 \in \mathcal{C}^1(\overline{\Omega})$.

(B2) $\mathbf{b}_1 \in \boldsymbol{\mathcal{C}^1}(\overline{\Omega})$
From (B1), the normal vector $\boldsymbol{\nu}$ belongs to $\boldsymbol{\mathcal{C}^1}(\partial\Omega)$ and so $\mathbf{b}_1(x) = d\boldsymbol{\nu}(x)$ can be extended to the whole $\overline{\Omega}$ with $\boldsymbol{\mathcal{C}^1}(\overline{\Omega})$ regularity.

(B3) Transversality condition:

$$\mathbf{b}_1(x) \cdot \boldsymbol{\nu}(x) = d\|\boldsymbol{\nu}(x)\|^2 = d > 0 \ \forall x \in \partial\Omega.$$

Remark 4.2.2. *We notice that the case of a cylindrical-3D reactor does not satisfy assumption (B1) as its boundary is not smooth enough (think on the circles where the bases and the lateral boundary meet).*

Hypothesis of function $\hat{\boldsymbol{\varphi}}$

Next, we will prove locally Lipschitz and Hölder properties of function $\hat{\boldsymbol{\varphi}}$ in problem (P_u) that will be stated in next Lemma 4.2.3 in a single inequality. They are needed in the local existence Theorem 4.2.1 below. Firstly, we need to prove two inequalities regarding locally Lipschitz (Lemma 4.2.1) and Hölder (Lemma 4.2.2) properties of function $\boldsymbol{\varphi}$ in problem (P).

Lemma 4.2.1. *In problem (P), function $\boldsymbol{\varphi}$ corresponding to the law of mass action satisfies the following locally Lipschitz property with respect to its third variable:*

For all $t \in [0,T]$, $x \in \Omega$, $\mathbf{y}_0 \in \mathbb{R}^N$ *and* $R > 0$ *there exists* $M(t,x,\mathbf{y}_0,R) > 0$ *such that*

$$\|\boldsymbol{\varphi}(t,x,\mathbf{y}_1) - \boldsymbol{\varphi}(t,x,\mathbf{y}_2)\| \leq M(t,x,\mathbf{y}_0,R)\|\mathbf{y}_1 - \mathbf{y}_2\| \quad \forall \mathbf{y}_1, \mathbf{y}_2 \in B(\mathbf{y}_0,R).$$

Furthermore, if $\theta \in \mathcal{C}([0,T]) \times \overline{\Omega})$ *and* $\theta(t,x) \neq 0$ $\forall (t,x) \in [0,T] \times \overline{\Omega}$, M *does not depend either on* t *or on* x.

Proof.
Let $\mathbf{y_0} \in \mathbb{R}^N$, $R > 0$ and $\mathbf{y}_1, \mathbf{y}_2 \in B(\mathbf{y_0}, R)$.

Then,

$$\begin{aligned}\|\boldsymbol{\varphi}(t,x,\mathbf{y}_1) - \boldsymbol{\varphi}(t,x,\mathbf{y}_2)\| &= \|A\boldsymbol{\delta}(t,x,\mathbf{y}_1) - A\boldsymbol{\delta}(t,x,\mathbf{y}_2)\| \\ &\leq \|A\|\|\boldsymbol{\delta}(t,x,\mathbf{y}_1) - \boldsymbol{\delta}(t,x,\mathbf{y}_2)\|.\end{aligned}$$

We define the following composition of functions

$$s \in [0,1] \xrightarrow{\zeta} \zeta(s) := s\mathbf{y}_1 + (1-s)\mathbf{y}_2 \in B(\mathbf{y}_1, R) \xrightarrow{\boldsymbol{\delta}(t,x,.)} \boldsymbol{\delta}(t,x,s\mathbf{y}_1 + (1-s)\mathbf{y}_2) \in \mathbb{R}^L.$$

Notice that $\boldsymbol{\delta}(t,x,\mathbf{y}_1) = \boldsymbol{\delta}(t,x,\zeta(1))$ and $\boldsymbol{\delta}(t,x,\mathbf{y}_2) = \boldsymbol{\delta}(t,x,\zeta(0))$. Then,

$$\|\boldsymbol{\varphi}(t,x,\mathbf{y}_1) - \boldsymbol{\varphi}(t,x,\mathbf{y}_2)\| \leq \|A\|\|\boldsymbol{\delta}(t,x,\zeta(1)) - \boldsymbol{\delta}(t,x,\zeta(0))\|. \tag{4.16}$$

Now, applying the Barrow Rule and the Chain Rule we get the following inequality:

$$\begin{aligned}\|\boldsymbol{\varphi}(t,x,\mathbf{y}_1) - \boldsymbol{\varphi}(t,x,\mathbf{y}_2)\| &\leq \|A\|\left\| \int_0^1 (\boldsymbol{\delta}(t,x,.) \circ \zeta)'(s) ds \right\| \\ &= \|A\|\left\| \int_0^1 D_{\mathbf{y}}\boldsymbol{\delta}(t,x,s\mathbf{y}_1 + (1-s)\mathbf{y}_2)(\mathbf{y}_1 - \mathbf{y}_2) ds \right\|.\end{aligned} \tag{4.17}$$

By operating with the second term on the left-hand side we obtain

$$\begin{aligned}&\left\| \int_0^1 D_{\mathbf{y}}\boldsymbol{\delta}(t,x,s\mathbf{y}_1 + (1-s)\mathbf{y}_2)(\mathbf{y}_1 - \mathbf{y}_2) ds \right\| \\ &\leq \int_0^1 \|D_{\mathbf{y}}\boldsymbol{\delta}(t,x,s\mathbf{y}_1 + (1-s)\mathbf{y}_2)(\mathbf{y}_1 - \mathbf{y}_2)\| ds \\ &\leq \int_0^1 \|D_{\mathbf{y}}\boldsymbol{\delta}(t,x,s\mathbf{y}_1 + (1-s)\mathbf{y}_2)\|\|\mathbf{y}_1 - \mathbf{y}_2\| ds \\ &\leq \Big(\int_0^1 \|D_{\mathbf{y}}\boldsymbol{\delta}(t,x,s\mathbf{y}_1 + (1-s)\mathbf{y}_2)\| ds \Big) \|\mathbf{y}_1 - \mathbf{y}_2\| \\ &\leq \Big(\sup_{0 \leq s \leq 1} \|D_{\mathbf{y}}\boldsymbol{\delta}(t,x,s\mathbf{y}_1 + (1-s)\mathbf{y}_2)\| \Big) \|\mathbf{y}_1 - \mathbf{y}_2\|.\end{aligned} \tag{4.18}$$

As $\mathbf{y}_1, \mathbf{y}_2 \in B(\mathbf{y}_0, R)$ and any ball is convex, then $s\mathbf{y}_1 + (1-s)\mathbf{y}_2 \in B(\mathbf{y}_0, R)$. Since $D_{\mathbf{y}}\boldsymbol{\delta}$ is continuous with respect to its third variable, by using Weierstrass' theorem we deduce that it is bounded on the ball and so,

$$\|\boldsymbol{\varphi}(t, x, \mathbf{y}_1) - \boldsymbol{\varphi}(t, x, \mathbf{y}_2)\| \leq M(t, x, \mathbf{y}_0, R)\|\mathbf{y}_1 - \mathbf{y}_2\|. \tag{4.19}$$

Moreover, if θ satisfies the above assumptions, the Arrhenius terms are bounded and hence,

$$L(\mathbf{y}_0, R) = \sup_{(t,x)\in[0,\tau]\times\overline{\Omega}} \sup_{0\leq s\leq 1} \|D_{\mathbf{y}}\boldsymbol{\delta}(t, x, s\mathbf{y}_1 + (1-s)\mathbf{y}_2)\| < \infty.$$

Finally,

$$\|\boldsymbol{\varphi}(t, x, \mathbf{y}_1) - \boldsymbol{\varphi}(t, x, \mathbf{y}_2)\| \leq L(\mathbf{y}_0, R)\|\mathbf{y}_1 - \mathbf{y}_2\|. \tag{4.20}$$

■

Lemma 4.2.2. *Let us assume that the temperature in the Arrhenius law belongs to the space $\mathcal{C}^1([0,T]) \times \overline{\Omega})$ and it is non-null $\forall (t,x) \in [0,T] \times \overline{\Omega}$. Then, function $\boldsymbol{\varphi}$ in problem (P) corresponding to law of mass action with Arrhenius law satisfies the following Hölder condition with respect to its first variable: there exists a constant C such that*

$$\|\boldsymbol{\varphi}(t, x, \mathbf{y}) - \boldsymbol{\varphi}(s, x, \mathbf{y})\| \leq C\|A\|\|\mathbf{h}(\mathbf{y})\||t - s| \quad \forall s, t \in [0,T] \ \forall \mathbf{y} \in \mathbb{R}^N,$$

where $h_l(\mathbf{y}) := \prod_{i=1}^{N} y_i^{\alpha_i^i}, \ l = 1, ..., L.$

Proof.
Let $0 \leq s < t \leq \tau$. Let us introduce the $L \times L$ diagonal matrix

$$E(t, x) := \begin{pmatrix} \exp\left(-\frac{E_{a1}}{\mathcal{R}\theta(t,x)}\right) & & \\ & \ddots & \\ & & \exp\left(-\frac{E_{aL}}{\mathcal{R}\theta(t,x)}\right) \end{pmatrix}.$$

Then we can write

$$\boldsymbol{\delta}(s, x, \mathbf{y}) = E(t, x)\mathbf{h}(\mathbf{y}),$$

Therefore,

$$\begin{aligned} \|\boldsymbol{\varphi}(t, x, \mathbf{y}) - \boldsymbol{\varphi}(s, x, \mathbf{y})\| &= \|AE(t, x)\mathbf{h}(\mathbf{y}) - AE(s, x)\mathbf{h}(\mathbf{y})\| \\ &\leq \|A\|\|E(t, x) - E(s, x)\|\|\mathbf{h}(\mathbf{y})\|. \end{aligned}$$

Moreover, it is easy to prove the following inequality via the Mean Value Theorem. By using the fact that θ and its derivative are continuous and bounded in a compact set and θ is not null, we have

$$\|E(t,x) - E(s,x)\| \leq C|t-s| \quad \forall t,s \in [0,T],\ x \in \overline{\Omega}.$$

Indeed, let us introduce the notation $\theta'(t,x) = \dfrac{\partial \theta}{\partial t}(x,t)$. Then, by the Mean Value Theorem we have

$$E_{ii}(t,x) - E_{ii}(s,x) = (t-s)\exp\left(-\frac{E_{ai}}{\mathcal{R}\theta(\zeta_i,x)}\right)E_{ai}\frac{\theta'(\zeta_i,x)}{\mathcal{R}\theta^2(\zeta_i,x)},$$

for some ζ_i between s and t, $\forall x \in \overline{\Omega}$ and $i = 1,...L$. Using that $\theta \in \mathcal{C}^1([0,T]\times\overline{\Omega})$ and $\theta \neq 0$, the absolute value of the the fraction

$$\frac{\theta'(\zeta_i,x)}{\mathcal{R}\theta^2(\zeta_i,x)}$$

can be bounded by taking the minimum value of θ^2 in the denominator and the maximum value of the absolute value of θ' in the numerator. Obviously the exponential is also bounded.

■

Now, it is the turn to study locally Lipschitz and Hölder properties for $\hat{\boldsymbol{\varphi}}$.

Lemma 4.2.3. *Under the assumptions*

- $\mathbf{g} \in \mathbf{W}^{2,r}(0,T;\mathbf{L}^p(\Gamma_1))$ *with* $p = n-1+\varepsilon$ *for* $n > 2$ *or* $\mathbf{g} \in \mathbf{W}^{2,r}(0,T;\mathbf{L}^2(\Gamma_1))$ *for* $n = 2$, *and* $r > 1$.
- *temperature* $\theta \in \mathcal{C}^1([0,T]) \times \overline{\Omega})$ *and* $\theta(t,x) \neq 0\ \forall (t,x) \in [0,T]\times\overline{\Omega}$,

function $\hat{\boldsymbol{\varphi}}$ *in problem* (P_u) *satisfies the following locally Lipschitz and Hölder property:*

For all $\mathbf{u}_0 \in \mathbb{R}^N$ *and* $R > 0$, *there exists* $P(\mathbf{u}_0, \mathbf{G}, R) > 0$ *such that,*

$$\|\hat{\boldsymbol{\varphi}}(t,x,\mathbf{u}_1) - \hat{\boldsymbol{\varphi}}(s,x,\mathbf{u}_2)\| \leq P(\mathbf{u}_o,\mathbf{G},R)\left(\|\mathbf{u}_1-\mathbf{u}_2\| + |t-s|^{\frac{r-1}{r}}\right), \quad (4.21)$$

for all $\mathbf{u}_1, \mathbf{u}_2 \in B(\mathbf{u_0}, R)$ *and for all* $s,t \in [0,T]$.

Proof. Firstly, let

$$m_G = \max_{(t,x)\in[0,\tau]\times\overline{\Omega}} \|\mathbf{G}(t,x)\|,$$

$\mathbf{u}_0 \in \mathbb{R}^N$ and R be any positive real number. Then,

$$\mathbf{u}_1 + \mathbf{G}(t,x),\ \mathbf{u}_2 + \mathbf{G}(t,x) \in B(\mathbf{u}_0, R + m_G)$$

for all $\mathbf{u}_1, \mathbf{u}_2 \in B(\mathbf{u}_0, R)$ and for all $(t, x) \in [0, \tau] \times \overline{\Omega}$.

Moreover, for $\hat{\boldsymbol{\varphi}}$ defined by (4.8) we have

$$\begin{aligned}
\|\hat{\boldsymbol{\varphi}}(t,x,\mathbf{u}_1) - \hat{\boldsymbol{\varphi}}(s,x,\mathbf{u}_2)\| &= \|\hat{\boldsymbol{\varphi}}(t,x,\mathbf{u}_1) - \hat{\boldsymbol{\varphi}}(t,x,\mathbf{u}_2) + \hat{\boldsymbol{\varphi}}(t,x,\mathbf{u}_2) - \hat{\boldsymbol{\varphi}}(s,x,\mathbf{u}_2)\| \\
&\leq \|\hat{\boldsymbol{\varphi}}(t,x,\mathbf{u}_1) - \hat{\boldsymbol{\varphi}}(t,x,\mathbf{u}_2)\| + \|\hat{\boldsymbol{\varphi}}(t,x,\mathbf{u}_2) - \hat{\boldsymbol{\varphi}}(s,x,\mathbf{u}_2)\| \\
&\leq \|\boldsymbol{\varphi}(t,x,\mathbf{u}_1 + \mathbf{G}(t,x)) - \boldsymbol{\varphi}(t,x,\mathbf{u}_2 + \mathbf{G}(t,x))\| \\
&\quad + \|\boldsymbol{\varphi}(t,x,\mathbf{u}_2 + \mathbf{G}(t,x)) - \boldsymbol{\varphi}(s,x,\mathbf{u}_2 + \mathbf{G}(s,x))\| \\
&\quad + \left\| \frac{\partial \mathbf{G}}{\partial t}(t,x) - \frac{\partial \mathbf{G}}{\partial t}(s,x) \right\| \\
&\leq \|\boldsymbol{\varphi}(t,x,\mathbf{u}_1 + \mathbf{G}(t,x)) - \boldsymbol{\varphi}(t,x,\mathbf{u}_2 + \mathbf{G}(t,x))\| \\
&\quad + \|\boldsymbol{\varphi}(t,x,\mathbf{u}_2 + \mathbf{G}(t,x)) - \boldsymbol{\varphi}(t,x,\mathbf{u}_2 + \mathbf{G}(s,x))\| \\
&\quad + \|\boldsymbol{\varphi}(t,x,\mathbf{u}_2 + \mathbf{G}(s,x)) - \boldsymbol{\varphi}(s,x,\mathbf{u}_2 + \mathbf{G}(s,x))\| \\
&\quad + \left\| \frac{\partial \mathbf{G}}{\partial t}(t,x) - \frac{\partial \mathbf{G}}{\partial t}(s,x) \right\|.
\end{aligned}$$

By using Lemma 4.2.1 and Lemma 4.2.2 we get

$$\begin{aligned}
\|\hat{\boldsymbol{\varphi}}(t,x,\mathbf{u}_1) - \hat{\boldsymbol{\varphi}}(s,x,\mathbf{u}_2)\| &\leq L(\mathbf{u}_0, R + m_G)\Big(\|\mathbf{u}_1 - \mathbf{u}_2\| + \|\mathbf{G}(t,x) - \mathbf{G}(s,x)\|\Big) \\
&\quad + C\|A\|\|\mathbf{h}(\mathbf{u}_2 + \mathbf{G}(s,x))\||t-s| + \left\| \frac{\partial \mathbf{G}}{\partial t}(t,x) - \frac{\partial \mathbf{G}}{\partial t}(s,x) \right\| \\
&\leq L(\mathbf{u}_0, R + m_G)\Big(\|\mathbf{u}_1 - \mathbf{u}_2\| + \|\mathbf{G}(t,x) - \mathbf{G}(s,x)\|\Big) \\
&\quad + Q(\mathbf{u}_0, R + m_G)|t-s| + \left\| \frac{\partial \mathbf{G}}{\partial t}(t,x) - \frac{\partial \mathbf{G}}{\partial t}(s,x) \right\|,
\end{aligned} \tag{4.22}$$

where

$$Q(\mathbf{u}_0, R + m_G) := C\|A\| \max\{\|\mathbf{h}(\mathbf{u})\| : \mathbf{u} \in B(\mathbf{u}_0, R + m_G)\}.$$

Notice that $\mathbf{G}$ and $\dfrac{\partial \mathbf{G}}{\partial t}$ are in $\mathcal{C}\big([0,\tau]; \boldsymbol{\mathcal{C}}(\overline{\Omega})\big)$. Hence $\mathbf{G}$ is continuously differentiable and then Lipschitz-continuous with respect to t. Moreover, if we repeat the argument in the proof of Proposition 4.2.1 for $\dfrac{\partial^2 \mathbf{G}}{\partial t^2}$, we obtain that $\dfrac{\partial \mathbf{G}}{\partial t} \in \mathbf{W}^{1,r}(0,T; \boldsymbol{\mathcal{C}}(\overline{\Omega}))$ and then it is Hölder with respect to t, with exponent

$\frac{r-1}{r}$. Indeed, we have

$$\left\|\frac{\partial \mathbf{G}}{\partial t}(t_2)-\frac{\partial \mathbf{G}}{\partial t}(t_1)\right\|_{\boldsymbol{\mathcal{C}}(\overline{\Omega})}=\left\|\int_{t_1}^{t_2}\frac{\partial^2 \mathbf{G}}{\partial t^2}(t)\,dt\right\|_{\boldsymbol{\mathcal{C}}(\overline{\Omega})}\leq\int_{t_1}^{t_2}\left\|\frac{\partial^2 \mathbf{G}}{\partial t^2}(t)\right\|_{\boldsymbol{\mathcal{C}}(\overline{\Omega})}dt$$
$$\leq (t_2-t_1)^{\frac{r-1}{r}}\Big(\int_{t_1}^{t_2}\left\|\frac{\partial^2 \mathbf{G}}{\partial t^2}(t)\right\|^r_{\boldsymbol{\mathcal{C}}(\overline{\Omega})}dt\Big)^{1/r}\leq C(t_2-t_1)^{\frac{r-1}{r}}.$$

Finally, this inequality and (4.22) yield (4.21).

■

Now, we state the local existence theorem for problem (P_u).

Theorem 4.2.1. *Assume that hypotheses (D1), (A1), (A2), as well as those in Lemma 4.2.3, hold. Let $\mathbf{u}_0 \in \boldsymbol{\mathcal{C}}(\overline{\Omega})$. Then,*

(i) there exists $\tau=\tau(\mathbf{u}_0)>0$ such that problem (P_u) has a unique classical solution $\mathbf{u}:[0,\tau]\times\overline{\Omega}\to\mathbb{R}^N$ with $\mathbf{u}\in\boldsymbol{\mathcal{C}}([0,\tau]\times\overline{\Omega})$.

(ii) $\mathbf{u}$ can be extended to a maximally defined solution

$$\mathbf{u}: I(\mathbf{u}_0)\times\overline{\Omega}\to\mathbb{R}^N,$$

$I(\mathbf{u}_0)$ being an interval starting in 0 and relatively open in $[0,T]$, i.e., either $I(\mathbf{u}_0)=[0,\tau)$ or $I(\mathbf{u}_0)=[0,\tau]$ with $\tau=T$.

Besides, $\mathbf{u}\in\mathcal{C}((0,\tau);D(\mathbf{A}))$ where $D(\mathbf{A})$ is defined in (4.14), $\mathbf{u}:(0,\tau)\to\boldsymbol{\mathcal{C}}(\overline{\Omega})$ is derivable and $\dfrac{\partial \mathbf{u}}{\partial t}$ and $A\mathbf{u}$ are continuous in $(0,\tau)\times\overline{\Omega}$.

Proof. It follows from results in Appendix B and it is divided in four steps:

First step. A is sectorial in $\mathbf{X}=\boldsymbol{\mathcal{C}}(\overline{\Omega})$

The realization $A_i: D(A_i)\to X$ of operator $\mathcal{A}_i$ in $X=\mathcal{C}(\overline{\Omega})$ with domain

$$D(A_i)=\{u\in\bigcap_{1\leq p<\infty}\mathbf{W}^{2,p}(\Omega):\mathcal{A}_i u\in X_i,\ \mathcal{B}_i u|_{\partial\Omega}=0\}$$

is sectorial in X thanks to Theorem B.3.1.

This means that, for each A_i there are constants $\omega_i\in\mathbb{R}$, $\dfrac{\pi}{2}<\theta_i<\pi$ and $M_i>0$ such that

(i) $\rho(A_i)\supset S_{\theta_i,\omega_i}=\{\lambda\in\mathbb{C}:\lambda\neq\omega_i, |arg(\lambda-\omega_i)|<\theta_i\}$;

(ii) $\|R(\lambda,A_i)\|_{L(X)}\leq\dfrac{M_i}{|\lambda-\omega_i|}\ \forall\lambda\in S_{\theta_i,\omega_i}$.

On the one hand, if we choose $\omega = \max_{i=1,\dots,N} \omega_i$ and $\theta = \min_{i=1,\dots,N} \theta_i$ for each $\lambda \in S_{\theta,\omega}$ we have that $\lambda \in \rho(A_i)\ \forall i = 1, ..., N$ and hence, $\lambda \in \rho(A)$.

On the other hand, from the definition of ω we have

$$|\lambda - \omega| \leq C_i |\lambda - \omega_i|$$

for some constant $C_i,\ i = 1, \dots, N$. Indeed, it is enough to take C_i as the real number

$$C_i = \sup_{\lambda \in \bar{S}_{\theta,\omega}} \left| \frac{\lambda - \omega}{\lambda - \omega_i} \right|.$$

We notice that C_i exists because function

$$\lambda \in \bar{S}_{\theta,\omega} \longrightarrow \frac{\lambda - \omega}{\lambda - \omega_i} \in \mathbb{C}$$

is continuous and $\lim_{|\lambda| \to \infty} \dfrac{\lambda - \omega}{\lambda - \omega_i} = 1$.

Then, we define $M = \max_{i=1,\dots,N} C_i M_i$ and thus $\|R(\lambda, A)\|_{L(\mathbf{X})} \leq \dfrac{M}{|\lambda - \omega|}$ $\forall \lambda \in S_{\theta,\omega}$.

Second step. Mapping $\hat{\mathbf{f}}$ in (4.13) is well-defined, continuous and for all $R > 0$ and $\mathbf{u_0} \in \mathbf{X}$ there exists $L > 0$ satisfying,

$$\|\hat{\mathbf{f}}(t, \mathbf{u}_1) - \hat{\mathbf{f}}(t, \mathbf{u}_2)\|_{\mathbf{X}} \leq L \|\mathbf{u_1} - \mathbf{u_2}\|_{\mathbf{X}} \quad \forall \mathbf{u_1}, \mathbf{u_2} \in B_{\mathbf{X}}(\mathbf{u_0}, R) \text{ and for } 0 \leq t \leq T.$$

Indeed, firstly for $t \in [0, T]$ and $\mathbf{u} \in \boldsymbol{\mathcal{C}}(\overline{\Omega})$ the function $x \in \overline{\Omega} \to \hat{\boldsymbol{\varphi}}(t, x, \mathbf{u}(x))$ is continuous and hence $\hat{\mathbf{f}}$ is well-defined. Moreover, the continuity in t for fixed $\mathbf{u}$ follows from Lemma 4.2.3.

Let $\mathbf{u}_1, \mathbf{u}_2 \in B_{\mathbf{X}}(\mathbf{u_0}, R)$ for some $R > 0$. Then,

$$\mathbf{u}_1(x),\ \mathbf{u}_2(x) \in B(\mathbf{0}\,, R + \|\mathbf{u}_0\|)\ \forall x \in \overline{\Omega}$$

and using Lemma 4.2.3 we get

$$\begin{aligned}
&\|\hat{\mathbf{f}}(t, \mathbf{u}_1) - \hat{\mathbf{f}}(t, \mathbf{u}_2)\|_{\mathbf{X}} = \max_{x \in \overline{\Omega}} \|\hat{\mathbf{f}}(t, \mathbf{u}_1)(x) - \hat{\mathbf{f}}(t, \mathbf{u}_2)(x)\| \\
&= \max_{x \in \overline{\Omega}} \|\hat{\boldsymbol{\varphi}}(t, x, \mathbf{u}_1(x)) - \hat{\boldsymbol{\varphi}}(t, x, \mathbf{u}_2(x))\| \leq \max_{x \in \overline{\Omega}} P(\mathbf{0}\,, \mathbf{G}, R + \|\mathbf{u}_0\|) \|\mathbf{u}_1(x) - \mathbf{u}_2(x)\| \\
&= P(\mathbf{0}\,, \mathbf{G}, R + \|\mathbf{u}_0\|) \|\mathbf{u}_1 - \mathbf{u}_2\|_{\mathbf{X}}.
\end{aligned}$$

Third step. $D(\mathbf{A})$ is dense in $\mathbf{X}$. This is a consequence of Theorem B.3.1.

Then, by using Theorem B.4.1, problem (P_u) has a unique mild solution.

Finally, by making an additional step we are able to prove that this solution is a classical solution.

Fourth step. There exists $\alpha \in (0,1)$ such that for all R we have

$$\|\hat{\mathbf{f}}(t,\mathbf{u}) - \hat{\mathbf{f}}(s,\mathbf{u})\| \leq C(R)(t-s)^{\alpha},\ 0 \leq s < t \leq T,$$

for some constant depending on R, $C(R)$ and for all $\mathbf{u} \in \mathbf{X}$ such that $\|\mathbf{u}\|_{\mathbf{X}} \leq R$.

Let $\mathbf{u} \in \mathbf{X}$. Then, from Lemma 4.2.3

$$\begin{aligned}\|\hat{\mathbf{f}}(t,\mathbf{u}) - \hat{\mathbf{f}}(s,\mathbf{u})\|_{\mathbf{X}} &= \max_{x\in\overline{\Omega}} \|\hat{\mathbf{f}}(t,\mathbf{u})(x) - \hat{\mathbf{f}}(s,\mathbf{u})(x)\| \\ &= \max_{x\in\overline{\Omega}} \|\hat{\boldsymbol{\varphi}}(t,x,\mathbf{u}(x)) - \hat{\boldsymbol{\varphi}}(s,x,\mathbf{u}(x))\| \\ &\leq \max_{x\in\overline{\Omega}} P(\mathbf{0},\mathbf{G},R)\Big(\|\mathbf{u}(x)-\mathbf{u}(x)\| + (t-s)^{\frac{r-1}{r}}\Big) = P(\mathbf{0},\mathbf{G},R)(t-s)^{\frac{r-1}{r}}.\end{aligned}$$

Therefore, by applying Theorem B.5.1 the mild solution of (P_u) is also a classical solution of our problem (P_u) which, in particular, implies the claimed regularity results.

The second part of the theorem easily follows from Proposition B.5.1.

■

The regularity obtained for the solution will be necessary in the next section to prove the existence of a global solution in $[0,T]$.

4.2.3 Local existence of solution to problem (4.3)–(4.4)

By using the above results we can prove a local existence theorem for the original problem (4.3)–(4.4).

Theorem 4.2.2 (**Local existence of solution**). *Assume that hypotheses (D1), (A1), (A2), as well as those in Lemma 4.2.3, hold. Let* $\mathbf{y_0} \in \mathbf{C}(\overline{\mathbf{\Omega}})$.

Then, there exists a unique weak solution of problem (4.3)–(4.4) that is continuous, $\mathbf{y} \in \mathcal{C}([0,\tau]\times\overline{\Omega})$*, where* $\tau < \sup I(\mathbf{u}_0)$ *with* $\mathbf{u}_0 = \mathbf{y}_0 - \mathbf{G}(0)$.

Proof. On the one hand, let us recall that $\mathbf{G} \in \mathcal{C}([0,T]\times\overline{\Omega})$ is the unique solution of

$$\int_{\Omega} \nabla\mathbf{G}\mathbf{v}\cdot\mathbf{w} + \int_{\Omega} d\nabla\mathbf{G} : \nabla\mathbf{w} - \int_{\Gamma_1} (\mathbf{v}\cdot\boldsymbol{\nu})\mathbf{G}\cdot\mathbf{w} = \int_{\Gamma_1} \mathbf{g}\cdot\mathbf{w} \quad \mathbf{w} \in \mathbf{H}^1(\Omega) \quad (4.23)$$

(see Proposition 4.2.1).

On the other hand, let $\mathbf{u} \in \mathcal{C}(I(\mathbf{u}_0)\times\overline{\Omega}) \cap \mathcal{C}(I(\mathbf{u}_0)\setminus\{0\}; \mathbf{W}^{2,p}(\Omega))$ be the

unique maximal solution of (P_u). Multiplying scalarly the PDE system in (P_u) by $\mathbf{w} \in \mathbf{H}^1(\Omega)$ and integrating in Ω we obtain

$$\frac{d}{dt}\int_\Omega \mathbf{u}\cdot\mathbf{w} + \int_\Omega \nabla\mathbf{u}\mathbf{v}\cdot\mathbf{w} - \int_\Omega d\Delta\mathbf{u}\cdot\mathbf{w} = \int_\Omega \hat{\boldsymbol{\varphi}}(t,x,\mathbf{u})\cdot\mathbf{w}\ \forall \mathbf{w}\in\mathbf{H}^1(\Omega).$$

Now, using a Green's formula and the definition of $\hat{\boldsymbol{\varphi}}$ we have,

$$\begin{aligned}\frac{d}{dt}\int_\Omega \mathbf{u}\cdot\mathbf{w} + \int_\Omega \nabla\mathbf{u}\mathbf{v}\cdot\mathbf{w} + \int_\Omega d\nabla\mathbf{u}:\nabla\mathbf{w} - \int_{\partial\Omega} d\frac{\partial\mathbf{u}}{\partial\boldsymbol{\nu}}\cdot\mathbf{w}\\ = \int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{u}+\mathbf{G})\cdot\mathbf{w} - \frac{d}{dt}\int_\Omega \mathbf{G}\cdot\mathbf{w}.\end{aligned}$$

Replacing boundary conditions and rearranging terms we obtain

$$\frac{d}{dt}\int_\Omega (\mathbf{u}+\mathbf{G})\cdot\mathbf{w} + \int_\Omega \nabla\mathbf{u}\mathbf{v}\cdot\mathbf{w} + \int_\Omega d\nabla\mathbf{u}:\nabla\mathbf{w} - \int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})\mathbf{u}\cdot\mathbf{w} = \int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{u}+\mathbf{G})\cdot\mathbf{w}. \tag{4.24}$$

Finally, by adding both variational formulations (4.23) and (4.24), we have

$$\begin{aligned}&\frac{d}{dt}\int_\Omega (\mathbf{u}+\mathbf{G})\cdot\mathbf{w} + \int_\Omega \nabla(\mathbf{u}+\mathbf{G})\mathbf{v}\cdot\mathbf{w} + \int_\Omega d\nabla(\mathbf{u}+\mathbf{G}):\nabla\mathbf{w}\\ &- \int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})(\mathbf{u}+\mathbf{G})\cdot\mathbf{w} = \int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{u}+\mathbf{G})\cdot\mathbf{w} + \int_{\Gamma_1}\mathbf{g}\cdot\mathbf{w}.\end{aligned}$$

Since $\mathbf{u}+\mathbf{G}$ is bounded in $[0,\tau]\times\overline{\Omega}$, for $\tau < \sup I(\mathbf{u}_0)$, the same is true for $\boldsymbol{\varphi}(t,x,\mathbf{u}+\mathbf{G})$. Then, by using also standard energy estimates, we can prove that $\mathbf{y} := \mathbf{u}+\mathbf{G} \in \boldsymbol{\mathcal{C}}([0,\tau]\times\overline{\Omega})\cap L^2((0,\tau);\mathbf{H}^1(\Omega))$ with $\dfrac{\partial\mathbf{y}}{\partial t} \in L^2((0,\tau;\mathbf{H}^1(\Omega)')$ and it is a solution in $(0,\tau)$ of the weak problem

$$\begin{aligned}&\langle\frac{\partial\mathbf{y}}{\partial t},\mathbf{w}\rangle + a(\mathbf{y},\mathbf{w}) = \int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{y})\cdot\mathbf{w} + \int_{\Gamma_1}\mathbf{g}\cdot\mathbf{w} \quad \mathbf{w}\in\mathbf{H}^1(\Omega),\\ &\mathbf{y}(0) = \mathbf{y}_0.\end{aligned}$$

Now, let us prove uniqueness. Assume there exist two local solutions $\mathbf{y}_i \in \boldsymbol{\mathcal{C}}([0,\tau_i]\times\overline{\Omega})\cap L^2((0,\tau_i);\mathbf{H}^1(\Omega))$, $i=1,2$, of (4.3). Then, we subtract the above weak formulation for $\mathbf{y}_1$ and $\mathbf{y}_2$ and use $\mathbf{w} = \mathbf{y}_1 - \mathbf{y}_2$ as test function to obtain

$$\langle\frac{\partial(\mathbf{y}_1-\mathbf{y}_2)}{\partial t},\mathbf{y}_1-\mathbf{y}_2\rangle + a(\mathbf{y}_1-\mathbf{y}_2,\mathbf{y}_1-\mathbf{y}_2) = \int_\Omega (\boldsymbol{\varphi}(t,x,\mathbf{y}_1)-\boldsymbol{\varphi}(t,x,\mathbf{y}_2))\cdot(\mathbf{y}_1-\mathbf{y}_2)$$

for all $t\in[0,\tau]$, where, $\tau = \min\{\tau_1,\tau_2\}$. Equivalently,

$$\frac{1}{2}\frac{d}{dt}\int_\Omega \|\mathbf{y}_1-\mathbf{y}_2\|^2+a(\mathbf{y}_1-\mathbf{y}_2,\mathbf{y}_1-\mathbf{y}_2)=\int_\Omega(\boldsymbol{\varphi}(t,x,\mathbf{y}_1)-\boldsymbol{\varphi}(t,x,\mathbf{y}_2))\cdot(\mathbf{y}_1-\mathbf{y}_2).$$

Due to the coerciveness of the bilinear form a that has been shown in the proof of Proposition 4.2.1 and since $\boldsymbol{\varphi}$ is locally Lipschitz with respect to its third variable (see Lemma 4.2.1), we can write

$$\frac{1}{2}\frac{d}{dt}\int_\Omega \|\mathbf{y}_1-\mathbf{y}_2\|^2+\beta\|\mathbf{y}_1-\mathbf{y}_2\|^2_{\mathbf{H}^1(\Omega)}\leq L(\mathbf{0}\,,m)\|\mathbf{y}_1-\mathbf{y}_2\|^2_{\mathbf{L}^2(\Omega)},$$

where

$$m=\max\{\|\mathbf{y}_1\|_{\mathcal{C}([0,\tau]\times\overline{\Omega})},\|\mathbf{y}_2\|_{\mathcal{C}([0,\tau]\times\overline{\Omega})}\}.$$

Hence,

$$\frac{1}{2}\frac{d}{dt}\int_\Omega \|\mathbf{y}_1-\mathbf{y}_2\|^2-L(\mathbf{0}\,,m)\|\mathbf{y}_1-\mathbf{y}_2\|^2_{\mathbf{L}^2(\Omega)}\leq 0.$$

Multiplying this equality by $2e^{-2L(\mathbf{0}\,,m)t}$ we deduce

$$\begin{aligned}\frac{d}{dt}\left(e^{-2L(\mathbf{0}\,,m)t}\|\mathbf{y}_1-\mathbf{y}_2\|^2_{\mathbf{L}^2(\Omega)}\right)&=e^{-2L(\mathbf{0}\,,m)t}\frac{d}{dt}\int_\Omega\|\mathbf{y}_1-\mathbf{y}_2\|^2\\&\quad-2L(\mathbf{0}\,,m)e^{-2L(\mathbf{0}\,,m)t}\|\mathbf{y}_1-\mathbf{y}_2\|^2_{\mathbf{L}^2(\Omega)}\leq 0.\end{aligned}$$

Finally, by integrating between 0 and $t\in(0,\tau]$ and using that $\mathbf{y}_1$ and $\mathbf{y}_2$ satisfy the same initial condition we get

$$e^{-2L(\mathbf{0}\,,m)t}\|\mathbf{y}_1(t)-\mathbf{y}_2(t)\|^2_{\mathbf{L}^2(\Omega)}\leq 0,$$

and hence $\mathbf{y}_1(t)=\mathbf{y}_2(t)\ \forall t\in[0,\tau]$.

■

4.2.4 The maximally defined solution

Since $\mathbf{G}$ is defined in the whole interval $[0,T]$ and $\mathbf{y}=\mathbf{u}+\mathbf{G}$, then for any $\mathbf{y}_0\in\boldsymbol{\mathcal{C}}(\overline{\Omega})$ there is a maximal solution of problem (4.3)–(4.4), $\mathbf{y}\in\mathcal{C}(I(\mathbf{u}_0);\boldsymbol{\mathcal{C}}(\overline{\Omega}))$, where $\mathbf{u}_0:=\mathbf{y}_0-\mathbf{G}(0)$).

We notice that this maximal solution could not be a solution of the weak problem in $I(\mathbf{u}_0)$ if $\mathbf{y}$ is not bounded as $\tau\to\sup I(\mathbf{u}_0)$. However, it is a weak solution in $(0,\sup I(\mathbf{u}_0)-\varepsilon)$ for all $\varepsilon>0$.

Moreover, from Proposition B.5.2 we deduce that two cases are possible:

- either the maximal solution is defined in the whole interval, i.e., $I(\mathbf{u}_0)=[0,T]$, (i.e., it is a global solution),
- or $I(\mathbf{u}_0)=[0,\tau)$ with $\tau\leq T$ and $\mathbf{y}(t)$ is unbounded as a mapping from $I(\mathbf{u}_0)$ to $\boldsymbol{\mathcal{C}}(\overline{\Omega})$.

4.3 Global existence of weak solution

In this section we study the existence of a global solution for the n-dimensional convection-diffusion-reaction system. It is necessary to prove that the local solution does not blow up in the interval $[0, T]$. In other words, we need to prove that any maximal local solution is bounded.

In this context, there are two main properties that will be exploited. They will be called properties **(P)** and **(M)**:

(P) The non-negativity of any solution of (4.3)–(4.4) is preserved along time.

(M) There are constants $\alpha_i > 0$ with $i = 1, ..., N$ such that

$$\boldsymbol{\varphi}(t, x, \mathbf{r}) \cdot \boldsymbol{\alpha} \leq 0 \quad \forall \mathbf{r} \in (\mathbb{R}^+)^N. \tag{4.25}$$

In the following, we prove that these properties are satisfied in the case under consideration as well as some preliminary results based on them. Later, they will be used to prove that the solution exists in the whole time interval $[0, T]$.

In this section, the following additional assumptions are made:

(H_1) The inlet Robin boundary data $\mathbf{g}$ has non-negative components in $[0, T] \times \Gamma_1$.

(H_2) The initial data $\mathbf{y}_0(x)$ has non-negative components $\forall x \in \overline{\Omega}$.

Now, we prove the positivity of solution, that is, property **(P)** holds. In fact, we prove that if the reaction term is quasi-positive, then property **(P)** is satisfied.

Definition 4.3.1. *The reaction term $\boldsymbol{\varphi}$ is called **quasi-positive** if, for all $i = 1, ..., N$,*

$$\varphi_i(t, x, r_1, ..., r_{i-1}, 0, r_{i+1}, ..., r_N) \geq 0 \quad \forall \mathbf{r} \in [0, \infty)^N \text{ a.e. in } [0, T] \times \Omega.$$

Let us recall that the law of mass action [31] yields the following expression for the velocity of the l-th reaction (see (1.3)):

$$\delta_l = k_l \prod_{j=1}^{N} y_j^{\alpha_j^l},$$

so, the source term can be written as

$$\boldsymbol{\varphi} = A\boldsymbol{\delta},$$

where A is the stoichiometric matrix of the system.

Lemma 4.3.1. *The reaction term $\boldsymbol{\varphi} = A\boldsymbol{\delta}$ is quasi-positive for reaction systems governed by the law of mass action.*

Proof. Firstly, we have

$$\varphi_i(t,x,r_1,...,r_{i-1},r_i,r_{i+1},...,r_N) = \sum_{l=1}^{L}(\lambda_i^l - \nu_i^l)\hat{k}_l(\theta(t,x))\prod_{j=1}^{N} r_j^{\alpha_j^l}, \quad (4.26)$$

where $\hat{k}_l(\theta(t,x)) \geq 0$ a.e. in $[0,T]\times\Omega$.

Now, let us assume that $r_i = 0$ and $r_j \geq 0$ for $j \neq i$. Then, for $l \in \{1,\ldots,L\}$ we have two possibilities:

- *The i-th species is a reactant in the l-th reaction*

  In this case, $\lambda_i^l = 0$ and $\nu_i^l > 0$. Hence,

  $$(\lambda_i^l - \nu_i^l)k_l(t,x)\prod_{j=1}^{N} r_j^{\alpha_j^l} = -\nu_i^l k_l(t,x)\prod_{j=1}^{N} r_j^{\alpha_j^l} = 0,$$

  because $r_i = 0$ and so $r_i^{\alpha_i^l} = 0$.

- *The i-th species is a product in the l-th reaction*

  In this case, $\lambda_i^l > 0$ and $\nu_i^l = 0$ and then $(\lambda_i^l - \nu_i^l)k_l(t,x)\prod_{j=1}^{N} r_j^{\alpha_j^l} \geq 0$.

■

Theorem 4.3.1 (Positivity of solution). *Let us assume (H_1) and (H_2) hold. If the reaction term is quasi-positive, then the maximal solution of problem (4.3)–(4.4) is non-negative along the time. This means that property* **(P)** *is satisfied.*

Proof. Let us recall that the positive part of $\mathbf{z} \in \mathbf{H}^1(\Omega)$ is defined by

$$(\mathbf{z}^+)_i(x) := z_i^+(x) = \max\{0, z_i(x)\}, \text{ a.e. in } \Omega.$$

Similarly, the negative part is

$$(\mathbf{z}^-)_i(x) := \max\{0, -z_i(x)\}.$$

Both $\mathbf{z}^+$ and $\mathbf{z}^-$ belong to $\mathbf{H}^1(\Omega)$ (see [62]). This is because the functions

$$s \in \mathbb{R} \mapsto s^{\pm} \in \mathbb{R}$$

are global contractions, i.e., globally Lipschitz with Lipschitz constant equal to 1 . Then the mapping,

$$\begin{aligned}\tilde{\boldsymbol{\varphi}} : [0,T] \times \overline{\Omega} \times \mathbb{R}^N &\mapsto \mathbb{R}^N \\ (t,x,\mathbf{z}) &\mapsto \boldsymbol{\varphi}(t,x,\mathbf{z}^+)\end{aligned}$$

has a similar property to (4.21) and therefore, the problem

$$\begin{aligned}\langle \frac{\partial \mathbf{z}}{\partial t}, \mathbf{w}\rangle + \int_\Omega \nabla \mathbf{z}\mathbf{v}\cdot\mathbf{w} + \int_\Omega d\nabla\mathbf{z} : \nabla\mathbf{w} - \int_{\Gamma_1} (\mathbf{v}\cdot\boldsymbol{\nu})\mathbf{z}\cdot\mathbf{w} \\ = \int_\Omega \tilde{\boldsymbol{\varphi}}(t,x,\mathbf{z})\cdot\mathbf{w} + \int_{\Gamma_1} \mathbf{g}\cdot\mathbf{w} \quad \forall \mathbf{w}\in \mathbf{H}^1(\Omega), \\ \mathbf{z}(0) = \mathbf{y}_0,\end{aligned}$$

has a unique local solution in the same way as problem (4.3)-(4.4). Selecting $\mathbf{w} = \mathbf{z}^-$ as test function we get

$$\begin{aligned}\langle \frac{\partial \mathbf{z}}{\partial t}, \mathbf{z}^-\rangle + \int_\Omega \nabla \mathbf{z}\mathbf{v}\cdot\mathbf{z}^- + \int_\Omega d\nabla\mathbf{z} : \nabla\mathbf{z}^- - \int_{\Gamma_1} (\mathbf{v}\cdot\boldsymbol{\nu})\mathbf{z}\cdot\mathbf{z}^- \\ = \int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{z}^+)\cdot\mathbf{z}^- + \int_{\Gamma_1} \mathbf{g}\cdot\mathbf{z}^-.\end{aligned}$$

By using that $\mathbf{z} = \mathbf{z}^+ - \mathbf{z}^-$, $\mathbf{z}^+ : \mathbf{z}^- = 0$, $\nabla\mathbf{z}^+ : \nabla\mathbf{z}^- = 0$ and also

$$\nabla \mathbf{z}\mathbf{v}\cdot\mathbf{z}^- = \mathbf{v}\cdot\nabla\mathbf{z}^T\mathbf{z}^- = -\mathbf{v}\cdot(\nabla\mathbf{z}^-)^T\mathbf{z}^- = -\mathbf{v}\cdot\frac{1}{2}\nabla(\|\mathbf{z}^-\|^2),$$

we deduce

$$\begin{aligned}-\frac{1}{2}\frac{d}{dt}\int_\Omega \|\mathbf{z}^-\|^2 - \int_\Omega \mathbf{v}\cdot\frac{1}{2}\nabla(\|\mathbf{z}^-\|^2) - \int_\Omega d\|\nabla\mathbf{z}^-\|^2 + \int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{z}^-\|^2 \\ = \int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{z}^+)\cdot\mathbf{z}^- + \int_{\Gamma_1}\mathbf{g}\cdot\mathbf{z}^-.\end{aligned}$$

Then, using a Green's formula and that div$\mathbf{v} = 0$, we obtain

$$\begin{aligned}-\frac{1}{2}\frac{d}{dt}\int_\Omega \|\mathbf{z}^-\|^2 - \frac{1}{2}\int_{\partial\Omega}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{z}^-\|^2 - \int_\Omega d\|\nabla\mathbf{z}^-\|^2 + \int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{z}^-\|^2 \\ = \int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{z}^+)\cdot\mathbf{z}^- + \int_{\Gamma_1}\mathbf{g}\cdot\mathbf{z}^-.\end{aligned}$$

By rearranging terms, and since $\mathbf{v}\cdot\boldsymbol{\nu} = 0$ in Γ_3, we get

$$-\frac{1}{2}\frac{d}{dt}\int_\Omega \|\mathbf{z}^-\|^2 - \frac{1}{2}\int_{\Gamma_2}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{z}^-\|^2 - \int_\Omega d\|\nabla\mathbf{z}^-\|^2 + \frac{1}{2}\int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{z}^-\|^2 - \int_{\Gamma_1}\mathbf{g}\cdot\mathbf{z}^- = \int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{z}^+)\cdot\mathbf{z}^-. \tag{4.27}$$

Now, we use the fact that

$$\int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{z}^+)\cdot\mathbf{z}^- \geq 0, \tag{4.28}$$

because $\boldsymbol{\varphi}$ is quasi-positive. Indeed, for all (t,x) and $i \in \{1,\dots,N\}$ we can distinguish two cases, depending on the sign of $z_i(t,x)$:

1) If $z_i(t,x) \geq 0$, then $z_i(t,x)^- = 0$ and $\varphi_i(t,x,\mathbf{z}^+(t,x))z_i(t,x)^- = 0$.

2) If $z_i(t,x) < 0$, then $z_i(t,x)^- = -z_i(t,x) > 0$. Besides, $z_i(t,x)^+ = 0$ and from the quasi-positiveness of $\boldsymbol{\varphi}$, we conclude that $\varphi_i(t,x,\mathbf{z}^+(x,t)) \geq 0$ and hence $\varphi_i(t,x,\mathbf{z}^+(x,t))z_i(t,x)^- \geq 0$.

Therefore, (4.28) holds. Moreover, since $\mathbf{g} \geq \mathbf{0}$, $\mathbf{v}\cdot\boldsymbol{\nu} \geq 0$ in Γ_2 and $\mathbf{v}\cdot\boldsymbol{\nu} \leq 0$ in Γ_1, we have

$$\int_{\Gamma_1}\mathbf{g}\cdot\mathbf{z}^- \geq 0, \quad \int_{\Gamma_2}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{z}^-\|^2 \geq 0 \quad \text{and} \quad \int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})\|\mathbf{z}^-\|^2 \leq 0.$$

Now, by using these inequalities in (4.27) we get

$$\frac{d}{dt}\int_\Omega \|\mathbf{z}^-\|^2 \leq 0. \tag{4.29}$$

Integrating this inequality in $(0,t)$ for any $t \in [0,\tau)$ and using the positivity of the initial condition (which implies $\mathbf{z}^-(0) = \mathbf{0}$), we obtain

$$\|\mathbf{z}^-(t)\|^2_{L^2(\Omega)} \leq 0. \tag{4.30}$$

Hence, $\mathbf{z}^-(t) = 0$ which implies that $\mathbf{z}(t)$ is non-negative in $[0,\tau)$. Therefore, $\mathbf{z}$ is also a solution of problem (4.3)–(4.4), but from uniqueness of local solution $\mathbf{z}$ must be equal to $\mathbf{y}$ so $\mathbf{y}$ is non-negative.

■

Now, we prove property **(M)**. We work in two steps. Firstly, we prove an equality which is valid for any real constants. After that, we will be able to prove **(M)** in the case of the law of mass action by substituting these constants by the molecular masses of the species in the mixture.

Lemma 4.3.2. *Let* $\mathbf{y}$ *be the maximal solution of problem* (4.3)–(4.4) *and* $\mathbf{a} \in \mathbb{R}^N$. *Then, the following equality holds for all* $t \in (0, \tau)$*:*

$$\frac{d}{dt}\int_\Omega \mathbf{y}\cdot\mathbf{a} + \int_{\Gamma_2}(\mathbf{v}\cdot\boldsymbol{\nu})\mathbf{y}\cdot\mathbf{a} = \int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{y})\cdot\mathbf{a} + \int_{\Gamma_1}\mathbf{g}\cdot\mathbf{a}. \tag{4.31}$$

Proof.

By selecting the test function $\mathbf{w} = \mathbf{a}$ in (4.3) we obtain the following equality:

$$\frac{d}{dt}\int_\Omega \mathbf{y}\cdot\mathbf{a} + \int_\Omega \nabla\mathbf{y}\mathbf{v}\cdot\mathbf{a} - \int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})\mathbf{y}\cdot\mathbf{a} = \int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{y})\cdot\mathbf{a} + \int_{\Gamma_1}\mathbf{g}\cdot\mathbf{a}. \tag{4.32}$$

Now, by using a Green's formula in the convection term we deduce

$$\begin{aligned}\int_\Omega \nabla\mathbf{y}\ \mathbf{v}\cdot\mathbf{a} &= \int_\Omega \mathbf{v}\cdot\nabla\mathbf{y}^T\mathbf{a} = \int_\Omega \mathbf{v}\cdot\nabla(\mathbf{y}\cdot\mathbf{a})\\ &= \int_{\partial\Omega}\mathbf{y}\cdot\mathbf{a}\,\mathbf{v}\cdot\boldsymbol{\nu} - \int_\Omega \mathrm{div}\mathbf{v}\,\mathbf{y}\cdot\mathbf{a} = \int_{\partial\Omega}\mathbf{y}\cdot\mathbf{a}\,\mathbf{v}\cdot\boldsymbol{\nu}.\end{aligned}$$

Then, equation (4.32) can be written as

$$\frac{d}{dt}\int_\Omega \mathbf{y}\cdot\mathbf{a} + \int_{\partial\Omega}\mathbf{y}\cdot\mathbf{a}\,\mathbf{v}\cdot\boldsymbol{\nu} - \int_{\Gamma_1}\mathbf{v}\cdot\boldsymbol{\nu}\,\mathbf{y}\cdot\mathbf{a} = \int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{y})\cdot\mathbf{a} + \int_{\Gamma_1}\mathbf{g}\cdot\mathbf{a}.$$

Finally, rearranging the terms and taking into account that $\mathbf{v}\cdot\boldsymbol{\nu} = 0$ on Γ_3 we obtain equation (4.31).

■

Lemma 4.3.3. *If the source term corresponds to the law of mass action* (1.3)*, then property* (**M**) *holds. More precisely, we have*

$$\boldsymbol{\varphi}(t,x,\mathbf{r})\cdot\boldsymbol{\mathcal{M}} = 0 \quad \forall \mathbf{r}\in\mathbb{R}^N, \tag{4.33}$$

where $\boldsymbol{\mathcal{M}}$ *is the vector of molecular masses.*

Proof. Let us choose $\boldsymbol{\alpha} = \boldsymbol{\mathcal{M}}$ in (4.25). Then,

$$\boldsymbol{\varphi}(t,x,\mathbf{r})\cdot\boldsymbol{\mathcal{M}} = A\boldsymbol{\delta}(t,x,\mathbf{r})\cdot\boldsymbol{\mathcal{M}} = \boldsymbol{\delta}(t,x,\mathbf{r})\cdot A^t\boldsymbol{\mathcal{M}} = 0,$$

because the mass conservation in each reaction implies that

$$(A^t\boldsymbol{\mathcal{M}})_l = \sum_{i=1}^N(\lambda_i^l - \nu_i^l)\mathcal{M}_i = 0 \quad \forall l = 1,\dots,L.$$

■

As a consequence of property **(M)**, the total mass is bounded by a constant which depends on the initial condition $\mathbf{y}_0$ and boundary function $\mathbf{g}$, as it is proved in Corollary 4.3.1 below (notice that the total mass is not conserved because the "reactor" is not closed). However, although this property suggests that no *blow-up* may occur in finite time, the $\mathbf{L}^\infty(\Omega)$-norm of the solution may blow up in finite time for polynomial two-dimensional systems satisfying properties **(P)** and **(M)**, as shown in [56].

Firstly, we notice that, since $\mathbf{y} \geq \mathbf{0}$, the total mass in Ω at time t is given by

$$\mathrm{m}(t,\Omega) := \int_\Omega \mathbf{y}(t,x)\cdot\boldsymbol{\mathcal{M}} = \|\mathbf{y}(t)\cdot\boldsymbol{\mathcal{M}}\|_{\mathrm{L}^1(\Omega)},\ \text{a.e. in } [0,\tau).$$

Corollary 4.3.1 (**Boundedness of the total mass**). *Let* $\mathbf{y}$ *be the maximal solution of problem* (4.3)–(4.4). *Then we have that*

$$\mathbf{y}\cdot\boldsymbol{\mathcal{M}} \in \mathrm{L}^\infty(0,\tau;\mathrm{L}^1(\Omega)).$$

Proof. From Lemma 4.3.2 for $\mathbf{a} = \boldsymbol{\mathcal{M}}$ and using property **(M)** in Lemma 4.3.3 we deduce

$$\frac{d}{dt}\int_\Omega \mathbf{y}\cdot\boldsymbol{\mathcal{M}} + \int_{\Gamma_2}(\mathbf{v}\cdot\boldsymbol{\nu})\mathbf{y}\cdot\boldsymbol{\mathcal{M}} = \int_{\Gamma_1}\mathbf{g}\cdot\boldsymbol{\mathcal{M}}.$$

Now, we apply Theorem 4.3.1 regarding the positivity of $\mathbf{y}$ and use the assumption $\mathbf{v}\cdot\boldsymbol{\nu} \geq 0$ on Γ_2, to get

$$\frac{d}{dt}\int_\Omega(\boldsymbol{\mathcal{M}}\cdot\mathbf{y}) \leq \int_{\Gamma_1}\mathbf{g}\cdot\boldsymbol{\mathcal{M}} \leq \|\boldsymbol{\mathcal{M}}\|\int_{\Gamma_1}\|\mathbf{g}\|. \tag{4.34}$$

Finally, by integrating in the interval $(0,t)$ with $0 < t < \tau$ and taking into account that the initial condition belongs to $\mathbf{L}^1(\Omega)$, we deduce

$$\|\boldsymbol{\mathcal{M}}\cdot\mathbf{y}(t)\|_{L^1(\Omega)} \leq C < \infty, \tag{4.35}$$

where

$$C := \|\boldsymbol{\mathcal{M}}\cdot\mathbf{y}_0\|_{L^1(\Omega)} + \|\boldsymbol{\mathcal{M}}\|\int_0^T \|\mathbf{g}(s)\|_{L^1(\Gamma_1)}ds.$$

■

A similar equality to (4.31) can be proved replacing $\mathbf{y}$ with $\mathbf{u}$.

Lemma 4.3.4. *Let* $\mathbf{u}$ *be the maximal local solution of problem* (PA_u) *and* $\psi \in H^1(\Omega)$*. Then, the following equality holds for all* $t \in (0, \tau)$*:*

$$\int_\Omega \frac{\partial(\boldsymbol{\mathcal{M}} \cdot \mathbf{u})}{\partial t}\psi + \int_\Omega \mathbf{v} \cdot \nabla(\boldsymbol{\mathcal{M}} \cdot \mathbf{u})\psi + \int_\Omega d\nabla(\boldsymbol{\mathcal{M}} \cdot \mathbf{u}) \cdot \nabla\psi$$
$$- \int_{\Gamma_1} (\mathbf{v} \cdot \boldsymbol{\nu})(\boldsymbol{\mathcal{M}} \cdot \mathbf{u})\psi = - \int_\Omega \frac{\partial \mathbf{G}}{\partial t} \cdot \mathcal{M}\psi \tag{4.36}$$

Proof. Firstly, we consider the weak formulation of problem (P_u), described in equation (4.24) and select as test function $\mathbf{w} = \boldsymbol{\mathcal{M}}\psi$, where $\psi \in H^1(\Omega)$. By taking into account Lemma 4.3.3 related to **(M)**, we obtain

$$\int_\Omega \frac{\partial(\boldsymbol{\mathcal{M}} \cdot \mathbf{u})}{\partial t}\psi + \int_\Omega \nabla\mathbf{u}\mathbf{v} \cdot \boldsymbol{\mathcal{M}}\psi + \int_\Omega d\nabla\mathbf{u} : \nabla(\boldsymbol{\mathcal{M}}\psi)$$
$$- \int_{\Gamma_1} (\mathbf{v} \cdot \boldsymbol{\nu})\mathbf{u} \cdot \boldsymbol{\mathcal{M}}\psi = - \int_\Omega \frac{\partial \mathbf{G}}{\partial t} \cdot \boldsymbol{\mathcal{M}}\psi, \tag{4.37}$$

where we have used the following equality:

$$\boldsymbol{\mathcal{M}} \cdot \hat{\boldsymbol{\varphi}}(t, x, \mathbf{u}) = \boldsymbol{\mathcal{M}} \cdot \boldsymbol{\varphi}(x, t, \mathbf{u} + \mathbf{G}) - \boldsymbol{\mathcal{M}} \cdot \frac{\partial \mathbf{G}}{\partial t}(t, x) = -\boldsymbol{\mathcal{M}} \cdot \frac{\partial \mathbf{G}}{\partial t}(t, x),$$

because of (4.33). Now, the second and the third terms in (4.37) can be transformed as follows

$$\int_\Omega \nabla\mathbf{u}\mathbf{v} \cdot \boldsymbol{\mathcal{M}}\psi = \int_\Omega \mathbf{v} \cdot \nabla\mathbf{u}^T \boldsymbol{\mathcal{M}}\psi = \int_\Omega \mathbf{v} \cdot \nabla(\boldsymbol{\mathcal{M}} \cdot \mathbf{u})\psi$$

and

$$\int_\Omega d\nabla\mathbf{u} : \nabla(\boldsymbol{\mathcal{M}}\psi) = \int_\Omega d\nabla\mathbf{u} : (\psi\nabla\boldsymbol{\mathcal{M}} + \boldsymbol{\mathcal{M}} \otimes \nabla\psi) = \int_\Omega d\nabla\mathbf{u} : (\boldsymbol{\mathcal{M}} \otimes \nabla\psi)$$
$$= \int_\Omega d\nabla(\boldsymbol{\mathcal{M}} \cdot \mathbf{u}) \cdot \nabla\psi,$$

because, in general,

$$S : (\mathbf{a} \otimes \mathbf{b}) = S^t\mathbf{a} \cdot \mathbf{b}$$

for any $N \times n$ matrix S, and vectors $\mathbf{a} \in \mathbb{R}^N$ and $\mathbf{b} \in \mathbb{R}^n$. By replacing in (4.37) we get the result.

■

Now, we study the global existence of solution using the above properties.

Proposition 4.3.1. *If properties* **(P)** *and* **(M)** *hold, as well as hypotheses* (H_1) *and* (H_2)*, then there exists a positive constant* C *such that the maximal solution satisfies*

$$\|\mathbf{y}\|_{\mathcal{C}([0,\tau]\times\overline{\Omega})} \leq C.$$

Proof. It is similar to the one showing the positivity of solution in Theorem 4.3.1.

Let M_1 and M_2 be any positive real numbers. From (4.36) it is easy to deduce that

$$\begin{aligned}
&\int_\Omega \frac{\partial(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)}{\partial t}\psi+\int_\Omega \mathbf{v}\cdot\nabla(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)\psi\\
&+\int_\Omega d\nabla(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)\cdot\nabla\psi-\int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)\psi\\
&=-\int_\Omega \frac{\partial\mathbf{G}}{\partial t}\cdot\boldsymbol{\mathcal{M}}\psi+\int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})(M_1+M_2t)\psi-M_2\int_\Omega\psi.
\end{aligned}$$

Now, let us choose $\psi=(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+$. We get

$$\begin{aligned}
&\frac{1}{2}\frac{d}{dt}\int_\Omega\left((\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+\right)^2\\
&+\int_\Omega \mathbf{v}\cdot\nabla(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+\\
&+\int_\Omega d\|\nabla(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+\|^2-\int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})\|(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+\|^2\\
&=-\int_\Omega\left(\frac{\partial\mathbf{G}}{\partial t}\cdot\boldsymbol{\mathcal{M}}+M_2\right)(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+\\
&+(M_1+M_2t)\int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+
\end{aligned}$$

and then

$$\begin{aligned}
&\frac{1}{2}\frac{d}{dt}\|(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}(t)-M_1-M_2t)^+\|^2_{L^2(\Omega)}+\int_\Omega d\|\nabla(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+\|^2\\
&+\frac{1}{2}\int_{\Gamma_2}\mathbf{v}\cdot\boldsymbol{\nu}\left((\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+\right)^2-\frac{1}{2}\int_{\Gamma_1}\mathbf{v}\cdot\boldsymbol{\nu}\left((\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+\right)^2\\
&=-\int_\Omega\left(\frac{\partial\mathbf{G}}{\partial t}\cdot\boldsymbol{\mathcal{M}}+M_2\right)(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+\\
&+(M_1+M_2t)\int_{\Gamma_1}(\mathbf{v}\cdot\boldsymbol{\nu})(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+.
\end{aligned}$$

Taking into account the sign of the different terms we deduce

$$\begin{aligned}
&\frac{1}{2}\frac{d}{dt}\|(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}(t)-M_1-M_2t)^+\|^2_{L^2(\Omega)}\\
&\leq-\int_\Omega\left(\frac{\partial\mathbf{G}}{\partial t}\cdot\boldsymbol{\mathcal{M}}+M_2\right)(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+ \qquad (4.38)
\end{aligned}$$

and integrating (4.38) in time from 0 to t we get

$$\begin{aligned}\|(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}(t)-M_1-M_2t)^+\|^2_{L^2(\Omega)} &\leq \|(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}_0-M_1)^+\|^2_{L^2(\Omega)}\\ -2\int_0^t\int_\Omega\left(\frac{\partial\mathbf{G}}{\partial t}\cdot\boldsymbol{\mathcal{M}}+M_2\right)&(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}-M_1-M_2t)^+.\end{aligned} \tag{4.39}$$

Now, let us take M_1 and M_2 such that

$$\boldsymbol{\mathcal{M}}\cdot\mathbf{u}_0(x)\leq M_1,\quad \left|\frac{\partial\mathbf{G}}{\partial t}(t,x)\cdot\boldsymbol{\mathcal{M}}\right|\leq M_2\ \ \forall t\in[0,T],\ \forall x\in\overline{\Omega}.$$

Then, (4.39) yields

$$\|(\boldsymbol{\mathcal{M}}\cdot\mathbf{u}(t)-M_1-M_2t)^+\|^2\leq 0$$

and finally,

$$\boldsymbol{\mathcal{M}}\cdot\mathbf{u}(t,x)\leq M_1+M_2T\ \ \forall t\in[0,T],\ \forall x\in\overline{\Omega},$$

from which it follows that

$$\boldsymbol{\mathcal{M}}\cdot\mathbf{y}(t,x)=\boldsymbol{\mathcal{M}}\cdot(\mathbf{u}(t,x)+\mathbf{G}(t,x))\leq M:=M_1+M_2T+\|\boldsymbol{\mathcal{M}}\cdot\mathbf{G}\|_{\mathcal{C}([0,T]\times\overline{\Omega})}.$$

From Theorem 4.3.1 the components of $\mathbf{y}$ are non-negative, so this inequality implies that

$$y_i(x,t)\leq\frac{M}{\mathcal{M}_i},\ i=1,\cdots,N,$$

which concludes the proof for

$$C=\max_{i=1,\ldots,N}\left\{\frac{M}{\mathcal{M}_i}\right\}.$$

■

Finally, we prove that the maximal solution is defined in the whole time interval $[0,T]$. That is, the solution can be prolonged to the space $\boldsymbol{\mathcal{C}}([0,T]\times\overline{\Omega})$. In the previous section, we have obtained the maximal interval for the local solution. From there, we are able to demonstrate that the solution is bounded in that interval, $I(\mathbf{y}_0)\subseteq[0,T]$. We argue by contradiction that the solution does not blow-up when it tends to T on the right side.

Theorem 4.3.2. *Under the assumptions (D1), (A1), (A2), (H1), (H2) and*

- $\mathbf{g}\in\mathbf{W}^{2,r}(0,\tau;\mathbf{L}^p(\Gamma_1))$ *with* $p=n-1+\varepsilon$ *if* $n>2$ *and* $p=2$ *if* $n=2$ *and* $r>1$,
- *temperature* $\theta\in\mathcal{C}^1([0,T])\times\overline{\Omega})$ *and* $\theta(t,x)\neq 0\ \forall(t,x)\in[0,T]\times\overline{\Omega}$,

there exists a global solution of problem (4.3)–(4.4) *(defined in* $[0,T]$*) such that* $\mathbf{y} \in \boldsymbol{\mathcal{C}}([0,T]\times\overline{\Omega})$.

Proof. It is a straightforward consequence of Proposition 4.3.1 and Proposition B.5.2 (see also Section 4.2.4).

■

4.3.1 Uniqueness of solution

As it is pointed out in [55] the question of uniqueness in general diffusion-reaction problems is certainly delicate since it is known that there is not uniqueness of weak solutions even for simple equations as, for instance,

$$\frac{\partial u}{\partial t} - \Delta u = u^3, u(0) = u_0 \geq 0, u = 0 \text{ on } \partial\Omega,$$

and even for $\mathcal{C}^\infty$ initial data. Further details can be found in [4] and [32].

However, working with uniformly bounded solutions is satisfactory because it allows us to prove uniqueness and so the problem is well posed in this class, as it is insured in [55]. Thus, we can conclude this chapter with the main result:

Theorem 4.3.3. *Under the assumptions in Theorem 4.3.2, there exists a unique bounded global solution in the interval* $[0,T]$ *of problem* (4.3)–(4.4).

Proof. Let as suppose that $\mathbf{y}_1, \mathbf{y}_2 \in \boldsymbol{\mathcal{C}}([0,T]\times\overline{\Omega})$ are solutions of (4.3)–(4.4). Then, for $i = 1, 2$, we have

$$\langle \frac{\partial \mathbf{y}_i}{\partial t}(t), \mathbf{w}\rangle + a(\mathbf{y}_i(t), \mathbf{w}) = \int_\Omega \boldsymbol{\varphi}(t,.,\mathbf{y}_i(t,.))\cdot\mathbf{w} + l(t)(\mathbf{w})$$
$$\forall \mathbf{w} \in \mathbf{H}^1(\Omega),$$
$$\mathbf{y}_i(0) = \mathbf{y}_0.$$

Now, if we subtract these formulations we obtain

$$\langle \frac{\partial(\mathbf{y}_1 - \mathbf{y}_2)}{\partial t}(t), \mathbf{w}\rangle + a(\mathbf{y}_1(t) - \mathbf{y}_2(t), \mathbf{w})$$
$$= \int_\Omega (\boldsymbol{\varphi}(t,.,\mathbf{y}_1(t,.)) - \boldsymbol{\varphi}(t,.,\mathbf{y}_2(t,.)))\cdot\mathbf{w}$$
$$\forall \mathbf{w} \in \mathbf{H}^1(\Omega),$$
$$\mathbf{y}_1(0) - \mathbf{y}_2(0) = \mathbf{0}.$$

By choosing $\mathbf{w} = \mathbf{y}_1(t) - \mathbf{y}_2(t)$ we get

$$\frac{1}{2}\frac{d}{dt}\|\mathbf{y}_1 - \mathbf{y}_2\|^2_{\mathbf{L}^2(\Omega)}(t) + a(\mathbf{y}_1(t) - \mathbf{y}_2(t), \mathbf{y}_1(t) - \mathbf{y}_2(t))$$
$$= \int_\Omega (\boldsymbol{\varphi}(t,.,\mathbf{y}_1(t,.) - \boldsymbol{\varphi}(t,.,\mathbf{y}_2(t,.)))\cdot\big(\mathbf{y}_1(t) - \mathbf{y}_2(t)\big).$$

Now, due to coerciveness of the bilinear form proved in Proposition 4.2.1 we can write

$$\frac{1}{2}\frac{d}{dt}\|\mathbf{y}_1-\mathbf{y}_2\|^2_{\mathbf{L}^2(\Omega)}+\beta\|\mathbf{y}_1(t)-\mathbf{y}_2(t)\|^2_{\mathbf{H}^1(\Omega)}$$
$$\leq\int_\Omega(\boldsymbol{\varphi}(t,.,\mathbf{y}_1(t,.))-\boldsymbol{\varphi}(t,.,\mathbf{y}_2(t,.)))\cdot\big(\mathbf{y}_1(t)-\mathbf{y}_2(t)\big).$$

Moreover, function $\boldsymbol{\varphi}$ is locally Lipschitz and hence it is Lipschitz in the union set of the ranges of the two solutions. Therefore, there exists, $K>0$ such that

$$\int_\Omega(\boldsymbol{\varphi}(t,.,\mathbf{y}_1(t,.))-\boldsymbol{\varphi}(t,.,\mathbf{y}_2(t,.)))\cdot\big(\mathbf{y}_1(t)-\mathbf{y}_2(t)\big)\leq K\|\mathbf{y}_1(t)-\mathbf{y}_2(t)\|^2_{L^2}$$

and then we can write

$$\frac{1}{2}\frac{d}{dt}\|\mathbf{y}_1-\mathbf{y}_2\|^2_{\mathbf{L}^2(\Omega)}(t)+\beta\|\mathbf{y}_1(t)-\mathbf{y}_2(t)\|^2_{\mathbf{H}^1(\Omega)}\leq K\|\mathbf{y}_1(t)-\mathbf{y}_2(t)\|^2_{\mathbf{L}^2(\Omega)}.$$

Finally, we integrate in $(0,t)$ to obtain the following inequality

$$\|\mathbf{y}_1(t)-\mathbf{y}_2(t)\|^2_{\mathbf{L}^2(\Omega)}\leq 2K\int_0^t\|\mathbf{y}_1(s)-\mathbf{y}_2(s)\|^2_{\mathbf{L}^2(\Omega)}$$

and by using the Gronwall's lemma, $\|\mathbf{y}_1(t)-\mathbf{y}_2(t)\|_{\mathbf{L}^2(\Omega)}\leq 0\ \forall t\in[0,T]$, so we can conclude that $\mathbf{y}_1=\mathbf{y}_2$ and hence the uniqueness.

■

Chapter 5

Numerical analysis of the convection-diffusion-reaction $n-$dimensional model

Convection-diffusion-reaction models are used in many applications in science and engineering. In general, these models are described by nonlinear equations for which an exact analytical solution is difficult to obtain, and from here the need of numerical methods in order to solve such non-linear models.

This chapter is devoted to the numerical solution of the problem introduced in the previous chapter, namely,

$$(P)\begin{cases} \dfrac{\partial \mathbf{y}}{\partial t}(t,x) + \nabla \mathbf{y}(t,x)\mathbf{v} - d\Delta \mathbf{y}(t,x) = \boldsymbol{\varphi}(t,x,\mathbf{y}(t,x)), \quad (t,x) \in (0,T)\times\Omega, \\ \mathbf{y}(0,x) = \mathbf{y}_0(x), \ x \in \Omega, \\ d\dfrac{\partial \mathbf{y}}{\partial \boldsymbol{\nu}}(t,x) - (\mathbf{v}(x)\cdot\boldsymbol{\nu}(x))\mathbf{y}(t,x) = \mathbf{g}(t,x), \quad (t,x) \in (0,T)\times\Gamma_1, \\ d\dfrac{\partial \mathbf{y}}{\partial \boldsymbol{\nu}}(t,x) = \mathbf{0}, \quad (t,x) \in (0,T)\times(\Gamma_2\cup\Gamma_3), \end{cases}$$

where Ω is a bounded domain in $\mathbb{R}^n$ with smooth boundary $\partial\Omega$.

Let us assume the hypotheses considered in Chapter 4 which are

- $d > 0$,
- $\mathbf{v} \in \mathcal{C}^1(\overline{\Omega})$, div$\mathbf{v} = 0$, $\mathbf{v}\cdot\boldsymbol{\nu} \leq 0$ on Γ_1, $\mathbf{v}\cdot\boldsymbol{\nu} \geq 0$ on Γ_2, $\mathbf{v}\cdot\boldsymbol{\nu} = 0$ on Γ_3,

and there exist $S \subset \Gamma_2$ with non-null surface measure and $\alpha > 0$ such that $\mathbf{v} \cdot \boldsymbol{\nu} \geq \alpha$ on S,

- $\mathbf{y}_0 \in \mathcal{C}(\overline{\Omega})$ with non-negative components $\forall x \in \overline{\Omega}$,
- $\mathbf{g} \in \mathbf{W}^{2,r}(0,T;\mathbf{L}^p(\Gamma_1))$ with $p = n-1+\varepsilon$ for $n > 2$ or $\mathbf{g} \in \mathbf{W}^{2,r}(0,T;\mathbf{L}^2(\Gamma_1))$ for $n = 2$, $r > 1$ and with non-negative components a.e. in $[0,T] \times \Gamma_1$,
- temperature $\theta \in \mathcal{C}^1([0,T]) \times \overline{\Omega})$ and $\theta(t,x) \neq 0 \ \forall (t,x) \in [0,T] \times \overline{\Omega}$.

Remark 5.0.1. *In next paragraphs, we assume that $\boldsymbol{\varphi} \in \mathcal{C}([0,T];\mathbf{H}^{l+1}(\Omega))$. In order to obtain the required regularity we must assume $\theta \in \mathcal{C}^1([0,T]);\mathcal{C}^{l+1}(\Omega))$. For the Law of Mass Action with integer coefficients the required regularity is insured.*

We recall that the non-negativity assumption of $\mathbf{g}$ and $\mathbf{y}_0$ has been described as (H1) and (H2).

Let us recall that the weak formulation of this problem consists in finding a function $\mathbf{y} \in L^2((0,T);\mathbf{H}^1(\Omega))$ satisfying

$$\frac{d}{dt}\int_\Omega \mathbf{y}(t,x)\cdot\mathbf{w}(x) + a(\mathbf{y}(t),\mathbf{w}) = \int_\Omega \boldsymbol{\varphi}(t,x,\mathbf{y}(t,x))\cdot\mathbf{w}(x) + l(t)(\mathbf{w})$$

$$\forall \mathbf{w} \in \mathbf{H}^1(\Omega) \quad (5.1)$$

$$\mathbf{y}(0) = \mathbf{y}_0, \quad (5.2)$$

where

$$a(\mathbf{y}(t),\mathbf{w}) := \int_\Omega \nabla\mathbf{y}(t,x)\mathbf{v}(x)\cdot\mathbf{w}(x) + \int_\Omega d\nabla\mathbf{y}(t,x) : \nabla\mathbf{w}(x) - \int_{\Gamma_1} (\mathbf{v}\cdot\boldsymbol{\nu})\mathbf{y}(t,x)\cdot\mathbf{w}(x)$$

and

$$l(t)(\mathbf{w}) := \int_{\Gamma_1} \mathbf{g}(t,x)\cdot\mathbf{w}(x).$$

5.1 The semidiscrete problem

This section is devoted first to build a semidiscrete problem obtained by replacing the Sobolev space $\mathbf{H}^1(\Omega)$ by a finite-dimensional approximation space and second to study the existence and uniqueness of a solution.

Firstly, we consider a linearly independent finite subset of the space $\mathrm{H}^1(\Omega) \cap \mathcal{C}(\overline{\Omega})$: $\{\psi_1, \cdots, \psi_{n_{dof}}\}$. Then, we introduce an associated approximation of $\mathbf{y}(t)$ in the space spanned by these functions, namely,

$$\hat{\mathbf{y}}(t) = \sum_{i=1}^{n_{dof}} \boldsymbol{\alpha}_i(t)\psi_i \in \mathbf{H}^1(\Omega) \cap \boldsymbol{\mathcal{C}}(\overline{\Omega}),$$

where $\boldsymbol{\alpha}_i(t),\ i = 1, \ldots, n_{dof}$ are some vector functions of time,

$$\boldsymbol{\alpha}_i : [0, T] \to \mathbb{R}^N,$$

to be determined.

Let us define the space spanned by $\{\psi_1, \cdots, \psi_{n_{dof}}\}$:

$$\widehat{\mathrm{W}} = \langle \psi_1, \cdots, \psi_{n_{dof}} \rangle$$

and let $\widehat{\mathbf{W}} = \widehat{\mathrm{W}}^N$. In order to define the approximation $\hat{\mathbf{y}}$, we go back to the weak formulation (5.1) and introduce the following problem:

Find a function $\hat{\mathbf{y}} : [0, T] \to \widehat{\mathbf{W}}$ *satisfying,*

$$\frac{d}{dt}\int_\Omega \hat{\mathbf{y}}(t) \cdot \mathbf{w} + a(\hat{\mathbf{y}}(t), \mathbf{w}) = \int_\Omega \boldsymbol{\varphi}(t, ., \hat{\mathbf{y}}(t)) \cdot \mathbf{w} + l(t)(\mathbf{w}),\ \forall \mathbf{w} \in \widehat{\mathbf{W}} \quad (5.3)$$

$$\hat{\mathbf{y}}(0) = \hat{\mathbf{y}}_0, \quad (5.4)$$

where $\hat{\mathbf{y}}_0$ *is a given approximation of* $\mathbf{y}_0$ *in* $\widehat{\mathbf{W}}$.

5.1.1 A finite element method

Here we introduce a particular but very important example of internal approximation space $\mathbf{V}_h$: let $\mathcal{T}_h$ be a collection of quasi-uniform elements (see Definition C.3.1) that partitions the domain $\Omega \subset \mathbb{R}^n$. These elements are triangles if $n = 2$ or tetrahedra if $n = 3$. Parameter h is the maximal diameter of the elements. Let us denote by $V = H^1(\Omega)$ and by V_h the space of piecewise continuous functions on Ω that reduce to polynomials of degree $\leq m$ on each element of $\mathcal{T}_h$.

Remark 5.1.1. *In the previous chapter we have supposed that* Ω *has a* $\mathcal{C}^2$ *boundary, for existence of a solution to the continuous problem (see 4.2.2). We notice that this assumption is not compatible with the fact that* Ω *has a partition in triangles or tetrahedra. Thus,* $V_h \not\subset V$ *and hence we are lead to commit a so-called variational crime in the Strang terminology. The error analysis arising from this variational crime is not trivial and it is beyond the scope of the present work.*

We consider the *canonical basis* of V_h, $\{\psi_{h,1}, \cdots, \psi_{h,n_{dof}}\}$, where $\psi_{h,i}$ has value 1 at the i-th node and 0 at the rest of the nodes. Then, the Lagrange interpolation operator,

$$\mathcal{I}_h : \mathcal{C}(\overline{\Omega}) \to V_h,$$

is defined as follows: $\mathcal{I}_h(f) \in V_h$ and

$$\mathcal{I}_h(f)(x_j) = f(x_j),$$

being $\{x_1, \ldots, x_{n_{dof}}\}$ the nodes associated to the finite element space (recall that in each element the set of nodes is the n-dimensional simplex of type m (see, for instance, [22]). Therefore,

$$\mathcal{I}_h(f) = \sum_{i=1}^{n_{dof}} f(x_i)\psi_{h,i}$$

and its extension to vector functions is straightforward:

$$\boldsymbol{\mathcal{I}}_h(\mathbf{f}) = (\mathcal{I}_h(f_1), \ldots, \mathcal{I}_h(f_N)).$$

Thus, we have

$$\boldsymbol{\mathcal{I}}_h(\mathbf{f}) = \sum_{i=1}^{n_{dof}} \mathbf{f}(x_i)\psi_{h,i}$$

and, in particular,

$$\boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(t, x, \mathbf{y}(t, x))\big) = \sum_{i=1}^{n_{dof}} \boldsymbol{\varphi}(t, x_i, \mathbf{y}(t, x_i))\psi_{h,i}(x). \tag{5.5}$$

Then, the finite element method with interpolated nonlinear term consists in

Finding

$$\mathbf{y}_h(t) = \sum_{i=1}^{n_{dof}} \boldsymbol{\alpha}_{h,i}(t)\psi_{h,i} \in \mathbf{V}_h$$

such that

$$\frac{d}{dt}\int_{\Omega_h} \mathbf{y}_h(t) \cdot \mathbf{w}_h + a(\mathbf{y}_h(t), \mathbf{w}_h)$$

$$= \int_{\Omega_h} \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(t, ., \mathbf{y}_h(t))\big) \cdot \mathbf{w}_h + l(t)(\mathbf{w}_h) \forall \mathbf{w}_h \in \mathbf{V}_h, \tag{5.6}$$

$$\mathbf{y}_h(0) = \mathbf{y}_{0,h}, \tag{5.7}$$

where

$$\mathbf{V}_h = (\mathrm{V}_h)^N$$

and $\mathbf{y}_{0,h}$ *is an approximation of* $\mathbf{y}_0$ *in* $\mathbf{V}_h$.

Now, we notice that the dimension of space $\mathbf{V}_h$ is $N \times n_{dof}$ and introduce a suitable basis for computer implementation:

$$\mathbf{z}_{h,nk} = \psi_{h,k}\mathbf{e}_n, \quad k = 1, ..., n_{dof} \text{ and } n = 1, ..., N,$$

where $\{\mathbf{e}_1, \cdots, \mathbf{e}_N\}$ is the canonical basis in $\mathbb{R}^N$.

Let us take $\mathbf{w}_h = \mathbf{z}_{h,nk}$. Then the nonlinear term can be written as

$$\int_{\Omega_h} \boldsymbol{\mathcal{I}}_h(\boldsymbol{\varphi}(t,.,\mathbf{y}_h(t)) \cdot \mathbf{z}_{h,nk} = \int_{\Omega_h} \boldsymbol{\mathcal{I}}_h(\boldsymbol{\varphi}(t,.,\mathbf{y}_h(t)) \cdot \mathbf{e}_n \psi_{h,k}$$
$$= \int_{\Omega_h} \mathcal{I}_h\big(\varphi_n(t,.,\mathbf{y}_h(t))\big)\psi_{h,k} = \sum_{i=1}^{n_{dof}} \int_{\Omega_h} \varphi_n\big(t, x_i, \boldsymbol{\alpha}_{h,i}(t)\big)\psi_{h,i}\psi_{h,k}$$
$$= \sum_{i=1}^{n_{dof}} \varphi_n\big(t, x_i, \boldsymbol{\alpha}_{h,i}(t)\big) \int_{\Omega_h} \psi_{h,i}\psi_{h,k}.$$

We notice that the obtained expression is the product of the mass matrix M_h defined by

$$M_{h,ik} = \int_{\Omega_h} \psi_{h,i}\psi_{h,k}, \ i,k = 1, \ldots, n_{dof},$$

times the vector

$$\boldsymbol{\varphi}_h^n(t) = \begin{pmatrix} \varphi_n\big(t, x_1, \boldsymbol{\alpha}_{h,1}(t)\big) \\ \vdots \\ \varphi_n\big(t, x_{n_{dof}}, \boldsymbol{\alpha}_{h,n_{dof}}(t)\big) \end{pmatrix}.$$

Now, we rewrite the above problem as a nonlinear numerical system. Let

$$\boldsymbol{\alpha}_h^n(t) = \begin{pmatrix} \alpha_{h,1}^n(t) \\ \vdots \\ \alpha_{h,n_{dof}}^n(t) \end{pmatrix} \in \mathbb{R}^{n_{dof}}$$

and

$$\boldsymbol{\alpha}_h(t) = \begin{pmatrix} \boldsymbol{\alpha}_h^1(t) \\ \vdots \\ \boldsymbol{\alpha}_h^N(t) \end{pmatrix} \in \mathbb{R}^{N n_{dof}}.$$

Then, the Cauchy problem to be solved is

$$\mathcal{M}_h \boldsymbol{\alpha}_h'(t) + \mathcal{A}_h \boldsymbol{\alpha}_h(t) = \mathcal{M}_h \boldsymbol{\varphi}_h(t, \boldsymbol{\alpha}_h(t)) + \mathbf{c}_h(t), \tag{5.8}$$
$$\boldsymbol{\alpha}_h(0) = \boldsymbol{\alpha}_{h,0}, \tag{5.9}$$

where $\mathcal{M}_h$ and $\mathcal{A}_h$ are block-diagonal matrices

$$\mathcal{M}_h = \begin{pmatrix} M_h & 0 & \cdots & 0 \\ 0 & M_h & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & M_h \end{pmatrix},$$

$$\mathcal{A}_h = \begin{pmatrix} A_h & 0 & \cdots & 0 \\ 0 & A_h & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & A_h \end{pmatrix},$$

because the corresponding terms in the original problem do not couple the components of $\mathbf{y}$. Each matrix block A_h is the stiffness matrix

$$A_{h,kj} = \int_{\Omega_h} \psi_{h,k}(\nabla\psi_{h,j} \cdot \mathbf{v}) + d\int_{\Omega_h} \nabla\psi_{h,j} \cdot \nabla\psi_{h,k} - \int_{\Gamma_1} (\mathbf{v} \cdot \boldsymbol{\nu})\psi_{h,j}\psi_{h,k},$$

with $k, j = 1, \cdots, n_{dof}$. Moreover,

$$\mathbf{c}_h^n(t) = \begin{pmatrix} c_{h,1}^n(t) \\ \vdots \\ c_{h,n_{dof}}^n(t) \end{pmatrix} \in \mathbb{R}^{n_{dof}},$$

and

$$\mathbf{c}_h(t) = \begin{pmatrix} \mathbf{c}_h^1(t) \\ \vdots \\ \mathbf{c}_h^N(t) \end{pmatrix} \in \mathbb{R}^{Nn_{dof}},$$

where

$$c_{h,k}^n(t) = \int_{\Omega_h} \psi_{h,k}(x) g_n(t,x),\ k = 1, \cdots, n_{dof} \text{ and } n = 1, \cdots, N$$

and

$$\boldsymbol{\varphi}_h(t, \boldsymbol{\alpha}_h(t)) = \begin{pmatrix} \boldsymbol{\varphi}_h^1(t, \boldsymbol{\alpha}_h(t)) \\ \vdots \\ \boldsymbol{\varphi}_h^N(t, \boldsymbol{\alpha}_h(t)) \end{pmatrix},$$

where

$$\boldsymbol{\varphi}_h^n(t, \boldsymbol{\alpha}_h(t)) = \begin{pmatrix} \varphi_{h,1}^n(t, \boldsymbol{\alpha}_{h,1}(t)) \\ \vdots \\ \varphi_{h,n_{dof}}^n(t, \boldsymbol{\alpha}_{h,n_{dof}}(t)) \end{pmatrix},$$

with $\varphi^n_{h,k}(t, \boldsymbol{\alpha}_{h,k}(t)) = \varphi_n\left(t, x_k, \boldsymbol{\alpha}_{h,k}(t)\right),\ k = 1, \dots n_{dof},\ n = 1, \dots, N.$

Finally, the initial condition is given by

$$\boldsymbol{\alpha}_{h,0} = \begin{pmatrix} \boldsymbol{\alpha}^1_{h,0} \\ \vdots \\ \boldsymbol{\alpha}^N_{h,0}, \end{pmatrix}$$

with

$$\mathbf{y}_{h,0} = \sum_{i=1}^{N} \boldsymbol{\alpha}^n_{h,0} \psi_{h,i}.$$

5.1.2 Local existence and uniqueness of solution to the semidiscrete problem

In this section, we study the existence and uniqueness of solution to the semidiscrete problem (5.6)–(5.7). This problem has been rewritten in the previous section as a nonlinear ordinary differential system in (5.8). The proof of existence of a local solution is based on the classical Picard-Lipschitz-Lindelöf theorem (see, for instance [23]). Let us first recall this theorem and then we will prove our local existence result.

Theorem 5.1.1 (Picard-Lipschitz-Lindelöf theorem). *Let $f : \mathcal{A} \subseteq \mathbb{R} \times \mathbb{R}^n \longrightarrow \mathbb{R}^n$ be a continuous function, locally Lipschitz with respect to x, where $\mathcal{A}$ is an open set.*

Then, for any given $(t_0, x_0) \in \mathcal{A}$, there exists a closed interval $I_\alpha = [t_0 - \alpha, t_0 + \alpha] \subset \mathbb{R}$ where the Cauchy problem:

$$\begin{aligned} x' &= f(t, x), \\ x(t_0) &= x_0, \end{aligned}$$

has a unique solution satisfying $(t, x(t)) \in \mathcal{A}\ \forall t \in I_\alpha$.

Now, we state the local existence of our ODEs system as follows:

Theorem 5.1.2. *There exists $\delta > 0$ such that the Cauchy problem (5.6)–(5.7) has a unique solution in the interval $(0, \delta)$.*

Proof.

Since the mass matrix $\mathcal{M}_h$ is invertible, the Cauchy problem (5.8)–(5.9) can be written as

$$\begin{aligned} \boldsymbol{\alpha}'_h(t) &= \boldsymbol{\varphi}_h(t, \boldsymbol{\alpha}_h(t)) + \mathcal{M}^{-1}\mathbf{c}_h(t) - \mathcal{M}^{-1}\mathcal{A}\boldsymbol{\alpha}_h(t), \\ \boldsymbol{\alpha}_h(0) &= \boldsymbol{\alpha}_{h,0}. \end{aligned}$$

Moreover, the mapping

$$(t, \boldsymbol{\alpha}_h) \to \boldsymbol{\varphi}_h(t, ., \boldsymbol{\alpha}_h) + \mathcal{M}_h^{-1}\mathbf{c}_h(t) - \mathcal{M}_h^{-1}\mathcal{A}_h\boldsymbol{\alpha}_h \in \mathbb{R}^{Nn_{dof}}$$

is continuous and locally Lipschitz with respect to $\boldsymbol{\alpha}_h$ from Lemma 4.2.1.

Therefore, by applying the Picard-Lipschitz-Lindelöf theorem, for $\boldsymbol{\alpha}_{h,0}$ given, this problem has a unique solution in $(0, \delta_h)$ for some $\delta_h \in (0, T]$.

■

Our next goal is to prove the existence of a global solution for the semidiscrete problem, i.e, a solution defined in the whole interval $[0, T]$. Firstly, we notice that the techniques used in the previous chapter to prove the global existence of solution to the continuous problem cannot be applied, essentially because for $\mathbf{w}_h \in \mathbf{V}_h$ its positive or negative parts do not belong, in general, to $\mathbf{V}_h$. This is why we will use a different method following some ideas from [63]. It consists in proving first an error estimate for the local solution in the L^∞-norm. Thus, since the solution of the continuous problem is bounded in $[0, T] \times \overline{\Omega}$, the same will be true for the local semidiscrete solution in the time interval of existence, for h small enough. This fact will allow us to prolong it to the whole interval $[0, T]$: let us assume that the maximal local solution for given h and $\mathbf{y}_{0,h}$ is defined in a time interval $I_h(\mathbf{y}_{0,h})$ starting at 0. Then, we will prove that, for h_0 small enough,

$$\sup_{t \in I_h(\mathbf{y}_{0,h})} \|\mathbf{y}_h(t)\| < \infty \ \forall h < h_0$$

and, therefore, well known results for ordinary differential equations will allow us to conclude that a global solution exists in $[0, T]$.

5.2 Error estimates for the semidiscrete solution

In this section we follow the lines of Thomee's book [63] in order to estimate the error obtained when the exact solution is replaced with the maximal numerical solution $\mathbf{y}_h : I_h(\mathbf{y}_{0,h}) \to \mathbf{V}_h$ of the semidiscrete problem

$$(\mathbf{y}_{h,t}, \boldsymbol{\chi}_h) + a(\mathbf{y}_h, \boldsymbol{\chi}_h) = (\boldsymbol{\mathcal{I}}_h(\boldsymbol{\varphi}(\mathbf{y}_h)), \boldsymbol{\chi}_h) + \int_{\Gamma_1} \mathbf{g} \cdot \boldsymbol{\chi}_h \ \forall \boldsymbol{\chi}_h \in \mathbf{V}_h,$$

where

$$\begin{aligned} a(\mathbf{y}_h, \boldsymbol{\chi}_h) :&= \int_\Omega \nabla \mathbf{y}_h \mathbf{v} \cdot \boldsymbol{\chi}_h + \int_\Omega d \nabla \mathbf{y}_h : \nabla \boldsymbol{\chi}_h - \int_{\Gamma_1} (\mathbf{v} \cdot \boldsymbol{\nu}) \mathbf{y} \cdot \boldsymbol{\chi}_h \\ &= (\nabla \mathbf{y}_h \mathbf{v}, \boldsymbol{\chi}_h) + d(\nabla \mathbf{y}_h, \nabla \boldsymbol{\chi}_h) - \int_{\Gamma_1} (\mathbf{v} \cdot \boldsymbol{\nu}) \mathbf{y}_h \cdot \boldsymbol{\chi}_h \end{aligned}$$

and $\mathbf{y}_h(0) = \mathbf{y}_{0h}$, with $\mathbf{y}_{0h} \in \mathbf{V}_h$ being an approximation of $\mathbf{y}_0$ in $\mathbf{V}_h$.

For the sake of simplicity, in this section we denote the derivative of a function φ with respect to t by $\varphi_{,t}$. Moreover, C will denote a constant may be different at each occurence.

For a given function $\mathbf{z} \in \mathbf{H}^1(\Omega)$, we recall that its elliptic projection onto $\mathbf{V}_h$ is the unique solution of the elliptic problem,

Find $\widetilde{\mathbf{z}}_h \in \mathbf{V}_h$ *such that*

$$a(\mathbf{z} - \widetilde{\mathbf{z}}_h, \boldsymbol{\chi}_h) = \mathbf{0} \quad \forall \boldsymbol{\chi}_h \in \mathbf{V}_h. \tag{5.10}$$

Then, we have the following result:

Lemma 5.2.1. *Let* $\widetilde{\mathbf{z}}_h \in \mathbf{V}_h$ *be the elliptic projection defined in* (5.10) *and assume* $\mathbf{z} \in \mathbf{H}^{l+1}(\Omega)$ *with* $l \leq m$. *Then,*

$$\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{L}^2(\Omega)} \leq Ch^{l+1}\|\mathbf{z}\|_{\mathbf{H}^{l+1}(\Omega)}. \tag{5.11}$$

Proof. Firstly, from the classical error estimates for elliptic problems based on Céa's Lemma, we have

$$\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{H}^1(\Omega)} \leq Ch^{l}\|\mathbf{z}\|_{\mathbf{H}^{l+1}(\Omega)}. \tag{5.12}$$

Then, in order to get (5.11) we use the Aubin-Nitsche technique (see, for instance, [37, Th. 3.37]). Let us call $\mathbf{e} \in \mathbf{H}^1(\Omega)$ the unique solution of the *adjoint* problem

$$a(\mathbf{w}, \mathbf{e}) = (\mathbf{z} - \widetilde{\mathbf{z}}_h, \mathbf{w})_{\mathbf{L}^2(\Omega)} \ \forall \mathbf{w} \in \mathbf{H}^1(\Omega). \tag{5.13}$$

From regularity results (see [30, Th. 2.4.2.7] or [37, Th. 3.18]) we have $\mathbf{e} \in \mathbf{H}^2(\Omega)$ and

$$\|\mathbf{e}\|_{\mathbf{H}^2(\Omega)} \leq C\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{L}^2(\Omega)}.$$

Let us take $\mathbf{w} = \mathbf{z} - \widetilde{\mathbf{z}}_h$ as test function in (5.13). We get,

$$\begin{aligned} \|\mathbf{z} - \widetilde{\mathbf{z}}_h\|^2_{\mathbf{L}^2(\Omega)} = a(\mathbf{z} - \widetilde{\mathbf{z}}_h, \mathbf{e}) = a(\mathbf{z} - \widetilde{\mathbf{z}}_h, \mathbf{e} - \boldsymbol{\mathcal{I}}_h(\mathbf{e})) \\ \leq C\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{H}^1(\Omega)}\|\mathbf{e} - \boldsymbol{\mathcal{I}}_h(\mathbf{e})\|_{\mathbf{H}^1(\Omega)} \leq C\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{H}^1(\Omega)}h\|\mathbf{e}\|_{\mathbf{H}^2(\Omega)} \\ \leq C\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{H}^1(\Omega)}h\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{L}^2(\Omega)} \end{aligned} \tag{5.14}$$

from which it follows that

$$\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{L}^2(\Omega)} \leq Ch\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{H}^1(\Omega)} \leq Ch^{l+1}\|\mathbf{z}\|_{\mathbf{H}^{l+1}(\Omega)}$$

by using (5.12).

Lemma 5.2.2. *Let* $\widetilde{\mathbf{z}}_h \in \mathbf{V}_h$ *be the elliptic projection defined in* (5.10) *and assume* $\mathbf{z} \in \mathbf{H}^{l+1}(\Omega)$ *with* $n/2 < l + 1 \leq m$. *Then,*

$$\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{L}^\infty(\Omega)} \leq C. \tag{5.15}$$

Proof. Firstly, we notice that $\mathbf{z} \in \mathbf{L}^\infty(\Omega)$ because $n/2 < l+1$. Moreover, from the triangular inequality we have

$$\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{L}^\infty(\Omega)} \leq \|\mathbf{z} - \mathcal{I}_h(\mathbf{z})\|_{\mathbf{L}^\infty(\Omega)} + \|\mathcal{I}_h(\mathbf{z}) - \widetilde{\mathbf{z}}_h\|_{\mathbf{L}^\infty(\Omega)}.$$

If we use Lemma C.3.2 in the first term and the inverse inequality (C.2) in the second one we deduce

$$\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{L}^\infty(\Omega)} \leq Ch^{l+1-\frac{n}{2}}\|\mathbf{z}\|_{\mathbf{H}^{l+1}(\Omega)} + Ch^{-\frac{n}{2}}\|\mathcal{I}_h(\mathbf{z}) - \widetilde{\mathbf{z}}_h\|_{\mathbf{L}^2(\Omega)} \tag{5.16}$$

and applying again the triangular inequality in the last term, and using Lemma C.3.2 and inequality (5.11) we can write

$$\begin{aligned} h^{-\frac{n}{2}}\|\mathcal{I}_h(\mathbf{z}) - \widetilde{\mathbf{z}}_h\|_{\mathbf{L}^2(\Omega)} &\leq h^{-\frac{n}{2}}\|\mathcal{I}_h(\mathbf{z}) - \mathbf{z}\|_{\mathbf{L}^2(\Omega)} + h^{-\frac{n}{2}}\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{L}^2(\Omega)} \\ &\leq Ch^{l+1-\frac{n}{2}}\|\mathbf{z}\|_{\mathbf{H}^{l+1}(\Omega)}. \end{aligned} \tag{5.17}$$

Finally, we derive the following $\mathbf{L}^\infty-$boundedness by substituting (5.17) in inequality (5.16):

$$\|\mathbf{z} - \widetilde{\mathbf{z}}_h\|_{\mathbf{L}^\infty(\Omega)} \leq Ch^{l+1-\frac{n}{2}}\|\mathbf{z}\|_{\mathbf{H}^{l+1}(\Omega)},$$

which implies (5.15) as $n/2 < l+1$.

■

Now we are in a position to prove the following error estimate for the semidiscrete solution.

Theorem 5.2.1. *Let us assume that the initial value $\mathbf{y}_0 \in \mathbf{H}^{l+1}(\Omega)$ and the global continuous solution has the following regularity properties:*

$$\mathbf{y} \in L^1((0,T);\mathbf{H}^{l+1}(\Omega)) \quad \mathbf{y}_{,t} \in L^1((0,T);\mathbf{H}^{l+1}(\Omega))$$

with $l+1 > n/2$ and $l \leq m$. Let $[0,\tau_h]$ be an interval where the local solution of the discrete problem is defined. Then,

$$\begin{aligned} &\|\mathbf{y} - \mathbf{y}_h\|_{L^\infty((0,\tau_h);\mathbf{L}^2(\Omega))} \leq C\|\mathbf{y}_0 - \mathbf{y}_{0h}\|_{\mathbf{L}^2(\Omega)} + Ch^{l+1}\|\mathbf{y}_0\|_{\mathbf{H}^{l+1}(\Omega)} \\ &+ Ch^{l+1}\left(1 + \|\mathbf{y}\|_{L^1((0,T);\mathbf{H}^{l+1}(\Omega))} + \|\mathbf{y}_{,t}\|_{L^1(0,T);\mathbf{H}^{l+1}(\Omega))}\right). \end{aligned} \tag{5.18}$$

Proof. Firstly, we split the error into two terms involving the elliptic projection of $\mathbf{y}$, $\widetilde{\mathbf{y}}_h$:

$$\mathbf{y} - \mathbf{y}_h = \boldsymbol{\rho_h} + \boldsymbol{\theta}_h,$$

with $\boldsymbol{\rho_h} = \mathbf{y} - \widetilde{\mathbf{y}}_h$ and $\boldsymbol{\theta}_h = \widetilde{\mathbf{y}}_h - \mathbf{y}_h$.

Then, we compare the elliptic projection, $\widetilde{\mathbf{y}}_h \in \mathbf{V}_h$, to the solution of the semidiscrete problem, i.e., we estimate $\boldsymbol{\theta}_h$. For this purpose, we notice that from our definitions,

$$\begin{aligned}
&\big(\boldsymbol{\theta}_{h,t}, \boldsymbol{\chi}_h\big) + a\left(\boldsymbol{\theta}_h, \boldsymbol{\chi}_h\right) = \left(\widetilde{\mathbf{y}}_{h,t}, \boldsymbol{\chi}_h\right) + a\left(\widetilde{\mathbf{y}}_h, \boldsymbol{\chi}_h\right) - \left(\mathbf{y}_{h,t}, \boldsymbol{\chi}_h\right) - a\left(\mathbf{y}_h, \boldsymbol{\chi}_h\right) \\
&= \left(\widetilde{\mathbf{y}}_{h,t}, \boldsymbol{\chi}_h\right) + a\left(\widetilde{\mathbf{y}}_h, \boldsymbol{\chi}_h\right) - \big(\boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y}_h)\big), \boldsymbol{\chi}_h\big) - \int_{\Gamma_1} \mathbf{g} \cdot \boldsymbol{\chi}_h \\
&= \langle \widetilde{\mathbf{y}}_{h,t} - \mathbf{y}_{,t} + \mathbf{y}_{,t}, \boldsymbol{\chi}_h\rangle + a\left(\mathbf{y}, \boldsymbol{\chi}_h\right) - \big(\boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y}_h)\big), \boldsymbol{\chi}_h\big) - \int_{\Gamma_1} \mathbf{g} \cdot \boldsymbol{\chi}_h \\
&= \langle \widetilde{\mathbf{y}}_{h,t} - \mathbf{y}_{,t}, \boldsymbol{\chi}_h\rangle + \left(\boldsymbol{\varphi}(\mathbf{y}), \boldsymbol{\chi}_h\right) - \big(\boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y}_h)\big), \boldsymbol{\chi}_h\big) \\
&= -(\boldsymbol{\rho}_{\boldsymbol{h},t}, \boldsymbol{\chi}_h) + \big(\boldsymbol{\varphi}(\mathbf{y}) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y}_h)\big), \boldsymbol{\chi}_h\big),
\end{aligned}$$

where $(\cdot,\cdot)$ represents the $\mathbf{L}^2(\Omega)$ inner product and we have assumed that $\mathbf{y}_{,t} \in L^2(0,T;\mathbf{L}^2(\Omega))$. Therefore,

$$\big(\boldsymbol{\theta}_{h,t}, \boldsymbol{\chi}_h\big) + a\left(\boldsymbol{\theta}_h, \boldsymbol{\chi}_h\right) = -(\boldsymbol{\rho}_{\boldsymbol{h},t}, \boldsymbol{\chi}_h) + \big(\boldsymbol{\varphi}(\mathbf{y}) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y}_h)\big), \boldsymbol{\chi}_h\big). \tag{5.19}$$

By choosing $\boldsymbol{\chi}_h = \boldsymbol{\theta}_h$, we rewrite equation (5.19) as

$$\frac{1}{2}\frac{d}{dt}\|\boldsymbol{\theta}_h\|^2_{\mathbf{L}^2(\Omega)} + a\left(\boldsymbol{\theta}_h, \boldsymbol{\theta}_h\right) = -\langle \boldsymbol{\rho}_{\boldsymbol{h},t}, \boldsymbol{\theta}_h\rangle + \big(\boldsymbol{\varphi}(\mathbf{y}) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y}_h)\big), \boldsymbol{\theta}_h\big).$$

Now, due to coerciveness of the bilinear form proved in Proposition 4.2.1 we can write

$$\frac{1}{2}\frac{d}{dt}\|\boldsymbol{\theta}_h\|^2_{\mathbf{L}^2(\Omega)} + \beta\|\boldsymbol{\theta}_h\|^2_{\mathbf{H}^1(\Omega)} \leq \|\boldsymbol{\rho}_{\boldsymbol{h},t}\|_{\mathbf{L}^2(\Omega)}\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)} + \big(\boldsymbol{\varphi}(\mathbf{y}) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y}_h)\big), \boldsymbol{\theta}_h\big)$$

and, by using that $\|\boldsymbol{\theta}_h\|^2_{\mathbf{L}^2(\Omega)} \leq \|\boldsymbol{\theta}_h\|^2_{\mathbf{H}^1(\Omega)}$, we get that

$$\frac{1}{2}\frac{d}{dt}\|\boldsymbol{\theta}_h\|^2_{\mathbf{L}^2(\Omega)} + \beta\|\boldsymbol{\theta}_h\|^2_{\mathbf{L}^2(\Omega)} \leq \|\boldsymbol{\rho}_{\boldsymbol{h},t}\|_{\mathbf{L}^2(\Omega)}\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)} + \big(\boldsymbol{\varphi}(\mathbf{y}) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y}_h)\big), \boldsymbol{\theta}_h\big). \tag{5.20}$$

The crucial issue in the error analysis is the interpolation error of the nonlinear term, that can be decomposed into three parts:

$$\begin{aligned}
\big(\boldsymbol{\varphi}(\mathbf{y}) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y}_h)\big), \boldsymbol{\theta}_h\big) &= \big(\boldsymbol{\varphi}(\mathbf{y}) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y})\big), \boldsymbol{\theta}_h\big) \\
+\big(\boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y})\big) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\widetilde{\mathbf{y}}_h)\big), \boldsymbol{\theta}_h\big) &+ \big(\boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\widetilde{\mathbf{y}}_h)\big) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y}_h)\big), \boldsymbol{\theta}_h\big).
\end{aligned}$$

By Cauchy–Schwartz inequality, we obtain

$$\begin{aligned}
\big(\boldsymbol{\varphi}(\mathbf{y}) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y}_h)\big), \boldsymbol{\theta}_h\big) \leq \Big(&\|\boldsymbol{\varphi}(\mathbf{y}) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y})\big)\|_{\mathbf{L}^2(\Omega)} \\
+\|\boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y})\big) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\widetilde{\mathbf{y}}_h)\big)\|_{\mathbf{L}^2(\Omega)} &+ \|\boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\widetilde{\mathbf{y}}_h)\big) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y}_h)\big)\|_{\mathbf{L}^2(\Omega)}\Big)\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)}.
\end{aligned}$$

For the first term, which is the interpolation error of $\boldsymbol{\varphi}(\mathbf{y})$, assuming that $\boldsymbol{\varphi}(\mathbf{y}) \in \mathcal{C}([0,T];\mathbf{H}^{l+1}(\Omega))$ and $1 \leq l \leq m$, we have (applying Remark C.3.2 in Appendix C)

$$\|\boldsymbol{\varphi}(\mathbf{y}) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y})\big)\|_{\mathbf{L}^2(\Omega)} \leq h^{l+1}\|\boldsymbol{\varphi}(\mathbf{y})\|_{\mathbf{H}^{l+1}(\Omega)} \leq Ch^{l+1}.$$

Now, for the second term, by using the locally-Lipschitz property of $\boldsymbol{\varphi}$ (with Lemma 5.2.2) and the inequalities from Lemma C.4.2, we have

$$\begin{aligned}
&\|\boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y})\big) - \boldsymbol{\mathcal{I}}_h\big(\big(\boldsymbol{\varphi}(\widetilde{\mathbf{y}}_h)\big)\|_{L^2(\Omega)} \leq C_2 h^{\frac{n}{2}}\|\boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\mathbf{y})\big) - \boldsymbol{\mathcal{I}}_h\big(\boldsymbol{\varphi}(\widetilde{\mathbf{y}}_h)\big)\|_h \\
&= C_2 h^{\frac{n}{2}}\|\boldsymbol{\varphi}(\mathbf{y}) - \boldsymbol{\varphi}(\widetilde{\mathbf{y}}_h)\|_h \leq C_3 h^{\frac{n}{2}} L\|\mathbf{y} - \widetilde{\mathbf{y}}_h\|_h = C_3 h^{\frac{n}{2}} L\|\boldsymbol{\mathcal{I}}_h\big(\mathbf{y}\big) - \widetilde{\mathbf{y}}_h\|_h \\
&\leq C_4 L\|\boldsymbol{\mathcal{I}}_h\big(\mathbf{y}\big) - \widetilde{\mathbf{y}}_h\|_{\mathbf{L}^2(\Omega)} \leq C_4 L\Big(\|\boldsymbol{\mathcal{I}}_h\big(\mathbf{y}\big) - \mathbf{y}\|_{\mathbf{L}^2(\Omega)} + \|\mathbf{y} - \widetilde{\mathbf{y}}_h\|_{\mathbf{L}^2(\Omega)}\Big) \\
&= C_4 L\Big(\|\boldsymbol{\mathcal{I}}_h\big(\mathbf{y}\big) - \mathbf{y}\|_{\mathbf{L}^2(\Omega)} + \|\boldsymbol{\rho_h}\|_{\mathbf{L}^2(\Omega)}\Big) \leq C_5\left(h^{l+1} + \|\boldsymbol{\rho_h}\|_{\mathbf{L}^2(\Omega)}\right).
\end{aligned}$$

For the third term, we apply the inequalities from Lemma C.4.2, equality (5.5) and the locally-Lipschitz property of $\boldsymbol{\varphi}$ to obtain

$$\begin{aligned}
&\|\boldsymbol{\mathcal{I}}_h\boldsymbol{\varphi}(\widetilde{\mathbf{y}}_h) - \boldsymbol{\mathcal{I}}_h\boldsymbol{\varphi}(\mathbf{y}_h)\|_{\mathbf{L}^2(\Omega)} \\
&\leq C_2 h^{\frac{n}{2}}\|\boldsymbol{\mathcal{I}}_h\boldsymbol{\varphi}(\widetilde{\mathbf{y}}_h) - \boldsymbol{\mathcal{I}}_h\boldsymbol{\varphi}(\mathbf{y}_h)\|_h = C_2 h^{\frac{n}{2}}\|\boldsymbol{\varphi}(\widetilde{\mathbf{y}}_h) - \boldsymbol{\varphi}(\mathbf{y}_h)\|_h \\
&\leq C_2 h^{\frac{n}{2}} L\|\widetilde{\mathbf{y}}_h - \mathbf{y}_h\|_h \leq C_3\|\widetilde{\mathbf{y}}_h - \mathbf{y}_h\|_{\mathbf{L}^2(\Omega)} = C_3\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)}.
\end{aligned}$$

In the previous estimates we have used that $\|\mathbf{y}_h(t)\|_{\mathbf{L}^\infty(\Omega)}$ is bounded in the time interval where we are working, i.e., in $[0,\tau_h]$.

Now, by replacing in inequality (5.20) we get

$$\begin{aligned}
\frac{1}{2}\frac{d}{dt}\|\boldsymbol{\theta}_h\|^2_{\mathbf{L}^2(\Omega)} + \beta\|\boldsymbol{\theta}_h\|^2_{\mathbf{L}^2(\Omega)} &\leq \|\boldsymbol{\rho}_{\boldsymbol{h},t}\|_{\mathbf{L}^2(\Omega)}\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)} \\
&+ \left(K_1 h^{l+1} + K_2\|\boldsymbol{\rho_h}\|_{\mathbf{L}^2(\Omega)} + K_3\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)}\right)\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)},
\end{aligned} \tag{5.21}$$

for some constants K_1, K_2, K_3.

Now, we have two possibilities:

- $\beta \geq K_3$: in this case we use the non-negativity of $\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)}$ and define $\lambda_2 := K_3$;
- $\beta < K_3$: in this case we define $\lambda_2 := K_3 - \beta > 0$.

In any case, we can write (5.21) as

$$\begin{aligned}
&\frac{1}{2}\frac{d}{dt}\|\boldsymbol{\theta}_h\|^2_{\mathbf{L}^2(\Omega)} \leq \|\boldsymbol{\rho}_{\boldsymbol{h},t}\|_{\mathbf{L}^2(\Omega)}\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)} \\
&+ \left(K_1 h^{l+1} + K_2\|\boldsymbol{\rho_h}\|_{\mathbf{L}^2(\Omega)} + \lambda_2\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)}\right)\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)},
\end{aligned}$$

or equivalently,

$$\begin{aligned}&\frac{1}{2}\frac{d}{dt}\|\boldsymbol{\theta}_h\|^2_{\mathbf{L}^2(\Omega)} - \lambda_2\|\boldsymbol{\theta}_h\|^2_{\mathbf{L}^2(\Omega)}\\&\leq \left(\|\boldsymbol{\rho}_{\boldsymbol{h},t}\|_{\mathbf{L}^2(\Omega)} + K_1 h^{l+1} + K_2\|\boldsymbol{\rho}_{\boldsymbol{h}}\|_{\mathbf{L}^2(\Omega)}\right)\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)}.\end{aligned} \tag{5.22}$$

Now we compute the following derivative

$$\frac{1}{2}\frac{d}{dt}\left(e^{-2\lambda_2 t}\|\boldsymbol{\theta}_h\|^2_{\mathbf{L}^2(\Omega)}\right) = e^{-2\lambda_2 t}\left(\frac{1}{2}\frac{d}{dt}\|\boldsymbol{\theta}_h\|^2_{\mathbf{L}^2(\Omega)} - \lambda_2\|\boldsymbol{\theta}_h\|^2_{\mathbf{L}^2(\Omega)}\right).$$

Then multiplying inequality (5.22) by $e^{-2\lambda_2 t}$ and using the above equality we obtain

$$\begin{aligned}&\frac{1}{2}\frac{d}{dt}\left(e^{-\lambda_2 t}\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)}\right)^2\\&\leq e^{-\lambda_2 t}\left(\|\boldsymbol{\rho}_{\boldsymbol{h},t}\|_{\mathbf{L}^2(\Omega)} + K_1 h^{l+1} + K_2\|\boldsymbol{\rho}_{\boldsymbol{h}}\|_{\mathbf{L}^2(\Omega)}\right)e^{-\lambda_2 t}\|\boldsymbol{\theta}_h\|_{\mathbf{L}^2(\Omega)}.\end{aligned}$$

By integrating in $(0,t)$ for $t<\tau_h$ we have

$$\begin{aligned}&\frac{1}{2}\left(e^{-\lambda_2 t}\|\boldsymbol{\theta}_h(t)\|_{\mathbf{L}^2(\Omega)}\right)^2 - \frac{1}{2}\|\boldsymbol{\theta}_h(0)\|^2_{\mathbf{L}^2(\Omega)}\\&\leq \int_0^t e^{-\lambda_2 s}\left(\|\boldsymbol{\rho}_{\boldsymbol{h},t}(s)\|_{\mathbf{L}^2(\Omega)} + K_1 h^{l+1} + K_2\|\boldsymbol{\rho}_{\boldsymbol{h}}(s)\|_{\mathbf{L}^2(\Omega)}\right)e^{-\lambda_2 s}\|\boldsymbol{\theta}_h(s)\|_{\mathbf{L}^2(\Omega)}ds\end{aligned}$$

and by applying [26, Lemma A.5] we obtain,

$$\begin{aligned}\|\boldsymbol{\theta}_h(t)\|_{\mathbf{L}^2(\Omega)} &\leq e^{\lambda_2 t}\|\boldsymbol{\theta}_h(0)\|_{\mathbf{L}^2(\Omega)}\\&\quad + e^{\lambda_2 t}\int_0^t e^{-\lambda_2 s}\left(\|\boldsymbol{\rho}_{\boldsymbol{h},t}(s)\|_{\mathbf{L}^2(\Omega)} + K_1 h^{l+1} + K_2\|\boldsymbol{\rho}_{\boldsymbol{h}}(s)\|_{\mathbf{L}^2(\Omega)}\right)ds.\end{aligned} \tag{5.23}$$

In order to estimate $\|\boldsymbol{\rho}_{\boldsymbol{h}}\|_{\mathbf{L}^2(\Omega)}$ and $\|\boldsymbol{\rho}_{\boldsymbol{h},t}\|_{\mathbf{L}^2(\Omega)}$ we use Lemma 5.2.1 for $\mathbf{z}=\mathbf{y}(t)$ and the fact that the time derivative of the elliptic projection is the elliptic projection of the time derivative (see, for instance, [58]). In other words, the following equality holds:

$$a\left(\frac{d\widetilde{\mathbf{y}}_h}{dt} - \frac{d\mathbf{y}}{dt}, \mathbf{z}\right) = 0 \ \forall \mathbf{z}\in\mathbf{H}^1(\Omega).$$

Thus, we obtain

$$\begin{aligned}&\|\boldsymbol{\rho}_{\boldsymbol{h}}\|_{\mathbf{L}^2(\Omega)} \leq Ch^{l+1}\|\mathbf{y}\|_{\mathbf{H}^{l+1}(\Omega)} \leq Ch^{l+1}\left(\|\mathbf{y}_0\|_{\mathbf{H}^{l+1}(\Omega)} + \int_0^t \|\mathbf{y}_{,t}\|_{\mathbf{H}^{l+1}(\Omega)}\right),\\&\|\boldsymbol{\rho}_{\boldsymbol{h},t}\|_{\mathbf{L}^2(\Omega)} \leq Ch^{l+1}\|\mathbf{y}_{,t}\|_{\mathbf{H}^{l+1}(\Omega)}.\end{aligned} \tag{5.24}$$

For $\|\boldsymbol{\theta}_h(0)\|_{\mathbf{L}^2(\Omega)}$ we have the following estimate by using Lemma 5.2.2

$$\begin{aligned}\|\boldsymbol{\theta}_h(0)\|_{\mathbf{L}^2(\Omega)} \leq & \|\widetilde{\mathbf{y}}_{0h} - \mathbf{y}_0\|_{\mathbf{L}^2(\Omega)} + \|\mathbf{y}_0 - \mathbf{y}_{0h}\|_{\mathbf{L}^2(\Omega)} \\ & \leq Ch^{l+1}\|\mathbf{y}_0\|_{\mathbf{H}^{l+1}(\Omega)} + \|\mathbf{y}_0 - \mathbf{y}_{0h}\|_{\mathbf{L}^2(\Omega)}.\end{aligned} \tag{5.25}$$

Now, using (5.24) and (5.25) in (5.23) we get

$$\begin{aligned}&\|\boldsymbol{\theta}_h(t)\|_{\mathbf{L}^2(\Omega)} \leq e^{\lambda_2 t}\|\mathbf{y}_0 - \mathbf{y}_{0h}\|_{\mathbf{L}^2(\Omega)} + Ch^{l+1}e^{\lambda_2 t}\|\mathbf{y}_0\|_{\mathbf{H}^{l+1}(\Omega)} \\ &+ e^{\lambda_2 t}\int_0^t e^{-\lambda_2 s}\left(K_1 h^{l+1} + K_4 h^{l+1}\|\mathbf{y}\|^2_{\mathbf{H}^{l+1}(\Omega)} + K_5 h^{l+1}\|\mathbf{y}_{,t}\|_{\mathbf{H}^{l+1}(\Omega)}\right).\end{aligned}$$

To conclude, the error estimate is given by the following inequality:

$$\begin{aligned}&\|\mathbf{y}(t) - \mathbf{y}_h(t)\|_{\mathbf{L}^2(\Omega)} \leq e^{\lambda_2 t}\|\mathbf{y}_0 - \mathbf{y}_{0h}\|_{\mathbf{L}^2(\Omega)} + K_6 h^{l+1}e^{\lambda_2 t}\|\mathbf{y}_0\|_{\mathbf{H}^{l+1}(\Omega)} \\ &+ K_7 h^{l+1}\|\mathbf{y}\|_{\mathbf{H}^{l+1}(\Omega)} + K_8 h^{l+1}e^{\lambda_2 t}\int_0^t e^{-\lambda_2 s}\left(1 + \|\mathbf{y}\|_{\mathbf{H}^{l+1}(\Omega)} + \|\mathbf{y}_{,t}\|_{\mathbf{H}^{l+1}(\Omega)}\right).\end{aligned}$$

■

5.3 Existence and uniqueness of global solution to the semidiscrete problem

In this section, by using the above error estimate, we prove the existence and uniqueness of a global solution to the semidiscrete problem (5.6)–(5.7). We recall that n denotes the spatial dimension, i.e., $\Omega \subset \mathbb{R}^n$.

Proposition 5.3.1. *Let us assume that*

- $\mathbf{y} \in L^1((0,T);\mathbf{H}^{l+1}(\Omega)), \quad \mathbf{y}_{,t} \in L^1((0,T);\mathbf{H}^{l+1}(\Omega))$.
- $l+1 > n/2$ *and* $l \leq m$.
- $\mathbf{y}_{0h}$ *is an approximation of* $\mathbf{y}_0$ *of order* $O(h^{n/2+\varepsilon})$ *in the norm of* $\mathbf{L}^2(\Omega)$, *for some* $\varepsilon > 0$.

Then the semidiscrete problem (5.6)–(5.7) *has a unique global solution* $\mathbf{y}_h \in \mathcal{C}^1([0,T];\mathbf{V}_h)$.

Proof. Since the global solution of the continuous problem, $\mathbf{y}$, is continuous in $[0,T]\times\overline{\Omega}$, the following real numbers,

$$m_i := \min\{y_i(t,x) : \ (t,x) \in [0,T]\times\overline{\Omega}\}, \tag{5.26}$$

$$M_i := \max\{y_i(t,x) : \ (t,x) \in [0,T]\times\overline{\Omega}\} \tag{5.27}$$

are well-defined for $i = 1, \ldots, N$.

Since we are assuming that the discrete initial condition satisfies

$$\|\mathbf{y}_0 - \mathbf{y}_{0h}\|_{\mathbf{L}^2(\Omega)} = O(h^{n/2+\varepsilon}), \tag{5.28}$$

by using Theorem 5.2.1 we obtain

$$\|\mathbf{y} - \mathbf{y}_h\|_{L^\infty((0,\tau_h(\mathbf{y}_{0,h}));\mathbf{L}^2(\Omega))} \leq O(h^{n/2+\varepsilon}) + O(h^{l+1}).$$

Besides, from Lemma C.3.2 we get

$$\|\boldsymbol{\mathcal{I}}_h\mathbf{y} - \mathbf{y}\|_{L^\infty((0,\tau_h(\mathbf{y}_{0,h}));\mathbf{L}^2(\Omega))} = O(h^{l+1})$$

and

$$\|\boldsymbol{\mathcal{I}}_h\mathbf{y} - \mathbf{y}\|_{L^\infty((0,\tau_h(\mathbf{y}_{0,h}));\boldsymbol{\mathcal{C}}(\overline{\Omega}))} = O(h^{l+1-n/2}).$$

Moreover, for all $t \in [0, \tau_h(\mathbf{y}_{0,h}))$

$$\begin{aligned}
\|\mathbf{y}(t) - \mathbf{y}_h(t)\|_{\boldsymbol{\mathcal{C}}(\overline{\Omega})} &\leq \|\mathbf{y}_h(t) - \boldsymbol{\mathcal{I}}_h\mathbf{y}(t)\|_{\boldsymbol{\mathcal{C}}(\overline{\Omega})} + \|\boldsymbol{\mathcal{I}}_h\mathbf{y}(t) - \mathbf{y}(t)\|_{\boldsymbol{\mathcal{C}}(\overline{\Omega})} \\
&\leq C_1 h^{-n/2}\|\mathbf{y}_h(t) - \boldsymbol{\mathcal{I}}_h\mathbf{y}(t)\|_{\mathbf{L}^2(\Omega)} + \|\boldsymbol{\mathcal{I}}_h\mathbf{y}(t) - \mathbf{y}(t)\|_{\boldsymbol{\mathcal{C}}(\overline{\Omega})} \\
&\leq C_1 h^{-n/2}\big(\|\mathbf{y}(t) - \mathbf{y}_h(t)\|_{\mathbf{L}^2(\Omega)} + \|\mathbf{y}(t) - \boldsymbol{\mathcal{I}}_h\mathbf{y}(t)\|_{\mathbf{L}^2(\Omega)}\big) \\
+\|\boldsymbol{\mathcal{I}}_h\mathbf{y}(t) - \mathbf{y}(t)\|_{\boldsymbol{\mathcal{C}}(\overline{\Omega})} &\leq C_1 h^{-n/2}\big(C_2 h^{n/2+\varepsilon} + C_3 h^{l+1}\big) + C_4 h^{l+1-n/2} \\
&= O(h^\varepsilon) + O(h^{l+1-n/2}),
\end{aligned}$$

where we have used the inverse inequality (C.2).

Therefore, for any $\delta > 0$ there exists $h_0 > 0$ such that for $h < h_0$ we have

$$m_i - \delta \leq y_{h,i}(t, x_j) \leq M_i + \delta \quad \forall t \in [0, \tau_h(\mathbf{y}_{0h})),\ j = 1, \ldots, n_{dof}$$

and then

$$\|\mathbf{y}_h(t)\|_{\mathcal{C}([0,\tau_h(\mathbf{y}_{0h}))\times\overline{\Omega})} \leq \max_{i=1,\ldots N} \max\{|m_i|, |M_i|\} + \delta.$$

This estimate and the classical theory of continuation of solutions of ordinary differential equations (see for example [23]) allow us to conclude that for $h < h_0$ there exists a global solution to the discrete problem belonging to the space $\mathcal{C}([0,T];\mathbf{V}_h)$. Now, since $\boldsymbol{\varphi}_h$ is continuous we deduce from (5.3) that $\dfrac{d\mathbf{y}_h}{dt}$ is also continuous.

Finally, the uniqueness can be proved as for the continuous problem in Theorem 4.3.3

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Chapter 6

Numerical solution of the PFR model

In Chapter 2 we have described the general model for a plug-flow reactor involving both species and temperature equations. These systems are usually stiff, and we should take this fact into account when choosing a numerical method. Stiff problems are characterized by large variations of the solution in a small time interval, hence most of the numerical methods must take small steps to obtain satisfactory results. This means that non-stiff methods can solve stiff problems, but they are time consuming. In this work we have selected a backward differentiation formula which is a simple and standard choice for solving stiff ordinary differential equations. More recent numerical discretizations based on Runge-Kutta schemes can be found, for instance in [33], where a method preserving the positivity of solution is included.

This chapter will be devoted to solve numerically the PFR model in both transient and steady state. Let us recall these problems:

$$(PFR)\begin{cases} \dfrac{\partial \mathbf{y}}{\partial t} + v\dfrac{\partial \mathbf{y}}{\partial z} - D\dfrac{\partial^2 \mathbf{y}}{\partial z^2} = A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}), \\ (\mathbf{w}'(\theta)\cdot \mathbf{y})\left(\dfrac{\partial \theta}{\partial t} + v\dfrac{\partial \theta}{\partial z}\right) - k\dfrac{\partial^2 \theta}{\partial z^2} = -\Delta\hat{\mathbf{H}}(\theta)\cdot\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) + \dfrac{2h}{R}(\theta_{ext} - \theta), \\ \mathbf{y}(z,0) = \mathbf{y}^0(z), \quad \theta(z,0) = \theta^0(z), \\ \mathbf{y}(0,t) \text{ and } \theta(0,t) \text{ given}, \\ \dfrac{\partial \mathbf{y}}{\partial z}(L,t) = 0, \quad \dfrac{\partial \theta}{\partial z}(L,t) = 0, \end{cases} \tag{6.1}$$

and

$$(PFR@SS)\begin{cases} v\dfrac{\partial \mathbf{y}}{\partial z} - D\dfrac{\partial^2 \mathbf{y}}{\partial z^2} = A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}), \\ (\mathbf{w}'(\theta)\cdot \mathbf{y})\left(v\dfrac{\partial \theta}{\partial z}\right) - k\dfrac{\partial^2 \theta}{\partial z^2} = -\Delta\hat{\mathbf{H}}(\theta)\cdot\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) + \dfrac{2h}{R}\,(\theta_{ext} - \theta), \\ \mathbf{y}(0) \text{ and } \theta(0) \text{ given}, \\ \dfrac{d\mathbf{y}}{dz}(L) = 0, \quad \dfrac{d\theta}{dz}(L) = 0. \end{cases} \tag{6.2}$$

6.1 Time and spatial discretizations of the problem

For numerical solution of the transient PFR model we propose the use of finite difference approximations for both space (z) and time (t) variables. Let us consider N_T time discretization steps and N_L spatial steps. We define time and spatial steps by

$$\Delta t = \frac{T}{N_T} \text{ and } \Delta z = \frac{L}{N_L - 1/2},$$

and time and spatial meshes by

$$t_n = n\Delta t,\ n = 1, \cdots, N_T \text{ and } z_j = j\Delta z,\ j = 0, \cdots, N_L + 1.$$

We notice that the last point in the spatial mesh is out of the interval $[0, L]$. More precisely,

$$z_{N_L} = N_L \Delta z = N_L \frac{L}{N_L - 1/2} = L + \frac{\Delta z}{2}.$$

Consequently, we use a second order approximation of the boundary condition on $z = L$ by taking a centred approximation of the first spatial derivative at this point.

Time discretization of the first order derivative in the convection term is the most delicate one in the system. This is because in a convection dominated problem (as it is the case for PFRs), a backward difference scheme to approximate this derivative is needed for the sake of stability. Otherwise, the time step must be very small. This is why we have implemented two kind of schemes: centred (order 2) and backward (of orders 1 and 2), as described below:

$$\frac{\partial \varphi}{\partial z}(z_j, t) \approx \frac{\varphi(z_j, t) - \varphi(z_{j-1}, t)}{\Delta z} \qquad \text{(backward formula of order 1)}$$

$$\frac{\partial \varphi}{\partial z}(z_j,t) \approx \frac{1.5\varphi(z_j,t) - 2\varphi(z_{j-1},t) + 0.5\varphi(z_{j-2},t)}{\Delta z},\ j = 2,\ldots,N_L$$

(backward formula of order 2)

$$\frac{\partial \varphi}{\partial z}(z_j,t) \approx \frac{\varphi(z_{j+1},t) - \varphi(z_{j-1},t)}{2\Delta z},\ j = 1,\ldots,N_L - 1$$

(centred formula of order 2).

The second order spatial derivative is approximated by the second order centred difference formula:

$$\frac{\partial^2 \varphi}{\partial z^2}(z_j,t) \approx \frac{\varphi(z_{j+1},t) - 2\varphi(z_j,t) + \varphi(z_{j-1},t)}{\Delta z^2},\ j = 1,\ldots,N_L - 1.$$

The integration in time is done step by step from $n = 1$ to $n = N_T$. The first step is computed using the implicit Euler scheme (which is also the first order *Backward Differentiation Formula*, BDF1) and the subsequent ones with the BDF2 (second order *Backward Differentiation Formula*) which was presented above for the spatial first derivative. Moreover, the boundary condition at the reactor outlet is replaced by the centred scheme.

In what follows we write the whole discretized problem with only the backward scheme of order 2 for the convection term.

1. First step, $n = 1$ (for $n = 0$ all values are known from the initial conditions).

$$\frac{\mathbf{y}_1^1 - \mathbf{y}_1^0}{\Delta t} + v\frac{\mathbf{y}_1^1 - \mathbf{y}_0^1}{\Delta z} - D\frac{\mathbf{y}_2^1 - 2\mathbf{y}_1^1 + \mathbf{y}_0^1}{\Delta z^2} = A\boldsymbol{\delta}(\theta_1^1, \mathbf{y}_1^1),$$

$$\frac{\mathbf{y}_j^1 - \mathbf{y}_j^0}{\Delta t} + v\frac{1.5\mathbf{y}_j^1 - 2\mathbf{y}_{j-1}^1 + 0.5\mathbf{y}_{j-2}^1}{\Delta z} - D\frac{\mathbf{y}_{j+1}^1 - 2\mathbf{y}_j^1 + \mathbf{y}_{j-1}^1}{\Delta z^2} = A\boldsymbol{\delta}(\theta_j^1, \mathbf{y}_j^1),$$
$$j = 2, \cdots, N_L,$$

$$\left(\mathbf{w}'(\theta_1^1)\cdot\mathbf{y}_1^1\right)\left(\frac{\theta_1^1 - \theta_1^0}{\Delta t} + v\frac{\theta_1^1 - \theta_0^1}{\Delta z}\right) - k\frac{\theta_2^1 - 2\theta_1^1 + \theta_0^1}{\Delta z}$$
$$= \frac{2h_{ext}}{R}\left(\theta_{ext}(t_1) - \theta_1^1\right) - \mathbf{w}(\theta_1^1)\cdot A\boldsymbol{\delta}(\theta_1^1, \mathbf{y}_1^1),$$

$$\left(\mathbf{w}'(\theta_j^1)\cdot\mathbf{y}_j^1\right)\left(\frac{\theta_j^1 - \theta_j^0}{\Delta t} + v\frac{\theta_j^1 - \theta_{j-1}^1}{\Delta z}\right) - k\frac{\theta_{j+1}^1 - 2\theta_j^1 + \theta_{j-1}^1}{\Delta z}$$
$$= \frac{2h_{ext}}{R}\left(\theta_{ext}(t_1) - \theta_j^1\right) - \mathbf{w}(\theta_j^1)\cdot A\boldsymbol{\delta}(\theta_j^1, \mathbf{y}_j^1),$$
$$j = 2, \cdots, N_L,$$

$$-d\frac{\mathbf{y}_1^1 - \mathbf{y}_0^1}{\Delta z} + v\frac{\mathbf{y}_0^1 + \mathbf{y}_1^1}{2} = v\mathbf{y}_{in}(t_1),$$

$$\frac{\theta_0^1 + \theta_1^1}{2} = \theta_{in}(t_1),$$

$$\frac{\mathbf{y}_{N_L+1}^1 - \mathbf{y}_{N_L}^1}{\Delta z} = \mathbf{0},$$

$$\frac{\theta_{N_L+1}^1 - \theta_{N_L}^1}{\Delta z} = 0.$$

2. Step $n \geq 2$ (all previous fields are known).

$$\frac{1.5\mathbf{y}_1^n - 2\mathbf{y}_1^{n-1} + 0.5\mathbf{y}_1^{n-2}}{\Delta t} + v\frac{\mathbf{y}_1^n - \mathbf{y}_0^n}{\Delta z} - D\frac{\mathbf{y}_2^n - 2\mathbf{y}_1^n + \mathbf{y}_0^n}{\Delta z} = A\boldsymbol{\delta}(\theta_1^n, \mathbf{y}_1^n),$$

$$\frac{1.5\mathbf{y}_1^n - 2\mathbf{y}_1^{n-1} + 0.5\mathbf{y}_1^{n-2}}{\Delta t} + v\frac{1.5\mathbf{y}_j^n - 2\mathbf{y}_{j-1}^n + 0.5\mathbf{y}_{j-2}^n}{\Delta z} - D\frac{\mathbf{y}_{j+1}^n - 2\mathbf{y}_j^n + \mathbf{y}_{j-1}^n}{\Delta z} = A\boldsymbol{\delta}(\theta_j^n, \mathbf{y}_j^n), \quad j = 2, \cdots, N_L,$$

$$(\mathbf{w}'(\theta_1^n) \cdot \mathbf{y}_1^n)\left(\frac{1.5\theta_j^n - 2\theta_j^{n-1} + 0.5\theta_j^{n-2}}{\Delta t} + v\frac{\theta_1^n - \theta_0^n}{\Delta z}\right) - k\frac{\theta_2^n - 2\theta_1^n + \theta_0^n}{\Delta z} = \frac{2h_{ext}}{R}\left(\theta_{ext}(t_n) - \theta_1^n\right) - \mathbf{w}(\theta_1^n) \cdot A\boldsymbol{\delta}(\theta_1^n, \mathbf{y}_1^n),$$

$$\left(\mathbf{w}'(\theta_j^n) \cdot \mathbf{y}_j^n\right)\left(\frac{1.5\theta_j^n - 2\theta_j^{n-1} + 0.5\theta_j^{n-2}}{\Delta t} + v\frac{\theta_j^n - \theta_{j-1}^n}{\Delta z}\right) - k\frac{\theta_{j+1}^n - 2\theta_j^n + \theta_{j-1}^n}{\Delta z} = \frac{2h_{ext}}{R}\left(\theta_{ext}(t_n) - \theta_j^n\right) - \mathbf{w}(\theta_j^n) \cdot A\boldsymbol{\delta}(\theta_j^n, \mathbf{y}_j^n), \quad j = 2, \cdots, N_L,$$

$$-d\frac{\mathbf{y}_1^n - \mathbf{y}_0^n}{\Delta z} + v\frac{\mathbf{y}_0^n + \mathbf{y}_1^n}{2} = v\mathbf{y}_{in}(t_n),$$

$$\frac{\theta_0^n + \theta_1^n}{2} = \theta_{in}(t_n),$$

$$\frac{\mathbf{y}_{N_L+1}^n - \mathbf{y}_{N_L}^n}{\Delta z} = \mathbf{0},$$

$$\frac{\theta_{N_L+1}^n - \theta_{N_L}^n}{\Delta z} = 0.$$

Let us notice that a nonlinear system of equations has to be solved at each time step. The number of equations of this system equals the number of

unknowns, which is $N_A \times N_L + (N+1) \times (N_L + 2)$.

6.2 Academic tests

Test at steady state

We use a simple model to construct this academic test. This is because we are only checking if the error reaches the expected order for the nonlinear functions we propose as solutions of the reaction system. Of course, this model involves equations of both species and temperature.

Then, let us consider a simple reaction system of three species $\{S_1, S_2, S_3\}$ involved in one chemical reaction:

$$S_1 + S_2 \rightarrow S_3, \tag{6.3}$$

and in terms of the stoichiometric matrix the reaction is represented as

$$A = \begin{pmatrix} -1 \\ -1 \\ 1 \end{pmatrix}. \tag{6.4}$$

The molecular mass of each species in $kg/kmol$ is given by the vector $\boldsymbol{\mathcal{M}} = (42, 138, 180)^t$ and the specific heat for all species is constant and equal, $c_{v_i} = 2.0\ 10^3\ J/kgK,\ i = 1, 2, 3$. We also assume identical diffusion term for all species equal to $d = 10^{-3}\ kg/kmol$. The effective coefficient of thermal conductivity is $k = 10^{-4}\ kg/kmol$ and the heat transfer coefficient between the reactor and its surroundings is null.

The law of mass action and the Arrhenius law are applied for modelling the kinetics. More precisely, the reaction term is given by

$$\delta_1 = B_1 \exp\left(\frac{Ea_1}{R\theta}\right) y_1 y_2, \tag{6.5}$$

where $B_1 = 3.0\ 10^7$ and $Ea_1 = 5.0\ 10^4$.

The heat of the reactions at temperature 298.15 K is 4.0 10^3 J/K. The volume of the reactor is 0.0029 m^3 and its length 1.5 m. The mixture velocity is constant and equal to 1.0 m/s There are no catalysts.

The exact solution of this problem is given by

$$\begin{aligned} y_1(z) &= e^{0.5z} + \cos^2 z, \\ y_2(z) &= e^{0.5z} + \sin^2 z, \\ y_3(z) &= e^z, \\ \theta(z) &= 298 + \sin^2 z. \end{aligned}$$

The boundary conditions are non-homogeneous and they have the following expressions:

$$
\begin{aligned}
y_{in_1} &= -0.5d + 2v, & y_{out_1} &= d(0.5e^{0.5} - 2\cos(1)\sin(1)),\\
y_{in_2} &= -0.5d + v, & y_{out_2} &= d(0.5e^{0.5} + 2\cos(1)\sin(1)),\\
y_{in_3} &= -d + v, & y_{out_3} &= de,\\
\theta_{in} &= 298. & \theta_{out} &= 2k\sin(1)\cos(1).
\end{aligned}
$$

With the complete information we can write the model we want to solve

$$
\begin{aligned}
v\frac{\partial \mathbf{y}}{\partial z} - d\frac{\partial^2 \mathbf{y}}{\partial z^2} &= A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) + \widetilde{\mathbf{f}} \text{ in } [0, L],\\
\left(\sum_{i=1}^{n} \mathcal{M}_i c_{v_i} y_i\right) v\frac{\partial \theta}{\partial z} - k\frac{\partial^2 \theta}{\partial z^2} &= -\Delta H(\theta)\cdot\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) + \frac{2h}{R}(\theta_{out} - \theta) + \widetilde{g} \text{ in } [0, L],\\
-d\frac{\partial \mathbf{y}}{\partial z}(0) + v\mathbf{y}(0) &= \mathbf{y}_{in} \text{ and } \frac{\partial \mathbf{y}}{\partial z}(L) = \mathbf{y}_{out},\\
\theta(0) &= \theta_{in} \text{ and } \frac{\partial \theta}{\partial z}(L) = \theta_{out}.
\end{aligned}
$$

We adjust $\widetilde{\mathbf{f}}$ and $\widetilde{g}$ in order to obtain the solution of the system described above, namely

$$
\begin{aligned}
\widetilde{f_1}(z) &= v(0.5e^{0.5z} - 2\sin z\cos z) - d(0.25e^{0.5z} + 2\sin^2 z - 2\cos z)\\
&-B_1\exp\left(\frac{Ea_1}{R\ (298 + \sin^2 z)}\right)(e^{0.5z} + \cos^2 z)(e^{0.5z} + \sin^2 z),
\end{aligned}
$$

$$
\begin{aligned}
\widetilde{f_2}(z) &= v(0.5e^{0.5z} + 2\sin z\cos z) - d(0.25e^{0.5z} - 2\sin^2 z + 2\cos z)\\
&-B_1\exp\left(\frac{Ea_1}{R\ (298 + \sin^2 z)}\right)(e^{0.5z} + \cos^2 z)(e^{0.5z} + \sin^2 z),
\end{aligned}
$$

$$
\widetilde{f_3}(z) = ve^z - de^z + B_1\exp\left(\frac{Ea_1}{R\ (298 + \sin^2 z)}\right)(e^{0.5z} + \cos^2 z)(e^{0.5z} + \sin^2 z),
$$

$$\widetilde{g}(z) = \left(\sum_{i=1}^{n} \mathcal{M}_i c_{v_i} y_i\right) v2 \sin z \cos z - 2k(\sin^2 z - \cos^2 z)$$
$$+\Delta H(\theta) B_1 \exp\left(\frac{Ea_1}{R\ (298 + \sin^2 z)}\right)(e^{0.5z} + \cos^2 z)(e^{0.5z} + \sin^2 z).$$

We have solved the problem in the space interval $[0, 1.5]$ for different step-sizes. The results are displayed in Table 6.1.

N_z	L^2 error for species	L^2 error for temperature
4	0.085818602	0.041901807
8	0.022819928	0.011007788
16	0.005975571	0.002881639
32	0.001532978	7.391990E-04
64	3.884191E-04	1.87E-04
128	9.78E-05	4.71E-05
256	2.45E-05	1.18E-05
512	6.14E-06	2.96E-06

Table 6.1: Table of errors in L^2 norm

This test was done using the centred scheme. We did not observe inconsistencies in the backward schemes. The error curves in logarithm scale are represented in Figure 6.1 and Figure 6.2 where it can be seen that the order of the expected error is 2 in both cases.

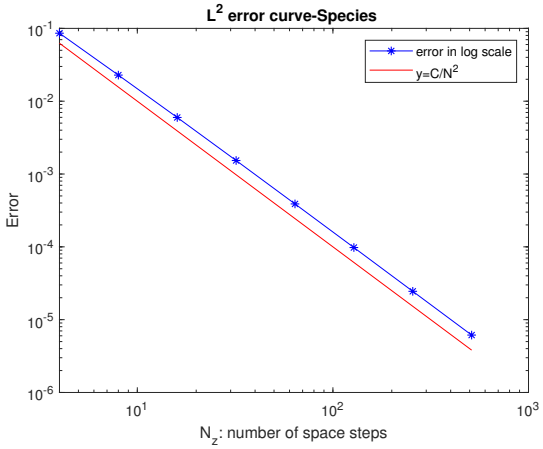

Figure 6.1: Species error for the steady state test

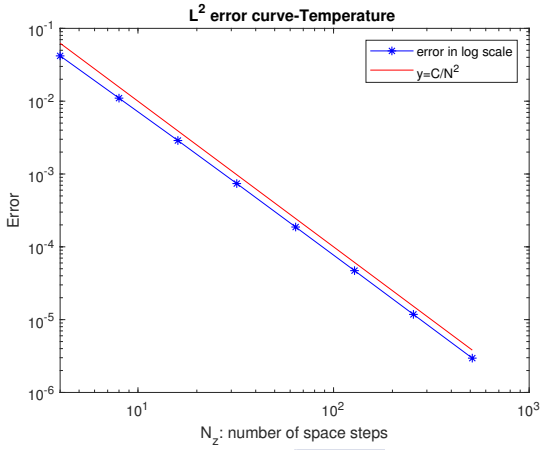

Figure 6.2: Temperature error for the steady state test

Test at transient state

Firstly, we test the time discretization scheme by solving a problem whose solution depends only on time variable. The selected test is the same as that used for steady state academic test, but replacing z with t. Thus, the exact solution is

$$\begin{aligned} y_1(z,t) &= e^{0.5t} + \cos^2 t, \\ y_2(z,t) &= e^{0.5t} + \sin^2 t, \\ y_3(z,t) &= e^{t}, \\ \theta(z,t) &= 298 + \sin^2 t. \end{aligned}$$

The boundary conditions have the following expressions:

$$\begin{aligned} y_{in_1}(t) &= v(e^{0.5t} + \cos^2 t), & y_{out_1}(t) &= 0, \\ y_{in_2}(t) &= v(e^{0.5t} + \sin^2 t), & y_{out_2}(t) &= 0, \\ y_{in_3}(t) &= ve^{t}, & y_{out_3}(t) &= 0, \\ \theta_{in}(t) &= 298 + \sin^2 t. & \theta_{out}(t) &= 0. \end{aligned}$$

Summarizing, we solve the problem

$$\frac{\partial \mathbf{y}}{\partial t} + v\frac{\partial \mathbf{y}}{\partial z} - d\frac{\partial^2 \mathbf{y}}{\partial z^2} = A\hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) + \widetilde{\mathbf{f}} \text{ in } [0,T]\times[0,L],$$

$$\sum_{i=1}^{n} \mathcal{M}_i c_{v_i} y_i \left(\frac{\partial \theta}{\partial t} + v\frac{\partial \theta}{\partial z}\right) - k\frac{\partial^2 \theta}{\partial z^2} = -\Delta H(\theta)\cdot \hat{\boldsymbol{\delta}}(\theta, \mathbf{y}) + \frac{2h}{R}(\theta_{out} - \theta) + \widetilde{g} \text{ in } [0,T]\times[0,L],$$

$$-d\frac{\partial \mathbf{y}}{\partial z}(0) + v\mathbf{y}(0) = \mathbf{y}_{in} \text{ and } \frac{\partial \mathbf{y}}{\partial z}(L) = \mathbf{y}_{out},$$

$$\theta(0) = \theta_{in} \text{ and } \frac{\partial \theta}{\partial z}(L) = \theta_{out}.$$

In order to obtain a solution, we adjust $\widetilde{\mathbf{f}}$ and $\widetilde{g}$ as following

$$\widetilde{f}_1(t) = (0.5e^{0.5t} - 2\sin(t)\cos t) - B_1 \exp\left(\frac{Ea_1}{R\,(298+\sin(t)^2)}\right)(e^{0.5t}+\cos^2 t)(e^{0.5t}+\sin^2 t),$$

$$\widetilde{f}_2(t) = (0.5e^{0.tz} + 2\sin t\cos t) - B_1 \exp\left(\frac{Ea_1}{R\,(298+\sin^2 t)}\right)(e^{0.5t}+\cos^2 t)(e^{0.5t}+\sin^2 t),$$

$$\widetilde{f}_3(t) = e^t + B_1 \exp\left(\frac{Ea_1}{R\,(298+\sin^2 t)}\right)(e^{0.5t}+\cos^2 t)(e^{0.5t}+\sin^2 t),$$

$$\widetilde{g}(t) = \left(\sum_{i=1}^{n}\mathcal{M}_i c_{v_i} y_i\right) 2\sin t\cos t + \Delta H(\theta) B_1 \exp\left(\frac{Ea_1}{R\,(298+\sin^2 t)}\right)(e^{0.5t}+\cos^2 t)(e^{0.5t}+\sin^2 t).$$

We solve the problem in the time interval $[0,1]$ and in the space interval $[0,1.5]$ for different step-sizes. We recall that the size of the spatial mesh does not modify the error because the exact solution is independent of the variable z. The results are displayed in Table 6.2.

N_t	L^2 error for species	L^2 error for temperature
4	0.027652771	0.002668311
8	0.005040992	0.000750139
16	0.000903504	0.000154572
32	0.000160727	2.90715E-05
64	2.8494E-05	5.29229E-06
128	5.04384E-06	9.49283E-07
256	8.92214E-07	1.69052E-07
512	1.57773E-07	2.9993E-08

Table 6.2: Table of errors in L^2 norm

In this case the error order we obtain is greater than 2 (2.38 approximately), as we can observe in the curves of the error in logarithm scale.

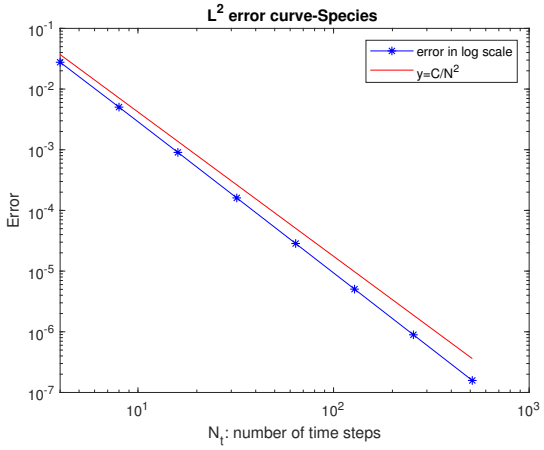

Figure 6.3: Species error in the transient state test

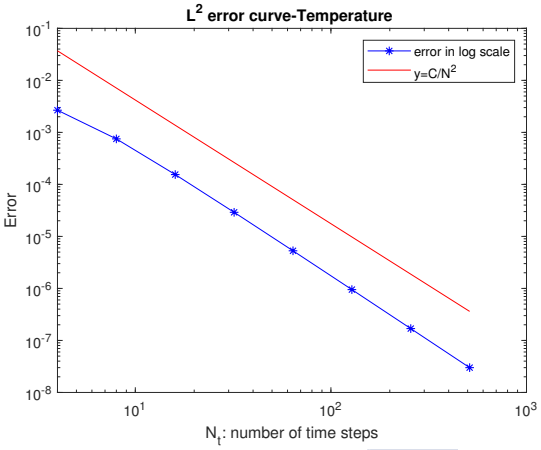

Figure 6.4: Temperature error in the transient state test

Now, we build a test whose solution depends on both variables (z, t). The test parameters are the same as in the previous one.

The exact solution is

$$
\begin{aligned}
y_1(z,t) &= e^{-t}(e^{0.5z} + \cos^2 z),\\
y_2(z,t) &= e^{-t}(e^{0.5z} + \sin^2 z),\\
y_3(z,t) &= e^{t}e^{z},\\
\theta(z,t) &= 298 + e^{-t}\sin^2 z.
\end{aligned}
$$

The boundary conditions have the following expressions:

$$
\begin{aligned}
y_{in_1} &= -0.5d + 2v, & y_{out_1} &= d(0.5e^{0.5} - 2\cos(1)\sin(1)),\\
y_{in_2} &= -0.5d + v, & y_{out_2} &= d(0.5e^{0.5} + 2\cos(1)\sin(1)),\\
y_{in_3} &= -d + v, & y_{out_3} &= de,\\
\theta_{in} &= 298. & \theta_{out} &= 2k\sin(1)\cos(1).
\end{aligned}
$$

In this case the auxiliary functions $\widetilde{\mathbf{f}}$ and $\widetilde{g}$ are given by

$$\widetilde{f}_1(z,t) = -e^{-t} + ve^{-t}(0.5e^{0.5z} - 2\sin z\cos z)$$
$$-de^{-t}(0.25e^{0.5z} + 2\sin^2 z - 2\cos z)$$
$$-B_1 \exp\left(\frac{Ea_1}{R\ (298 + e^{-t}\sin^2 z)}\right) e^{-2t}(e^{0.5z} + \cos^2 z)(e^{0.5z} + \sin^2 z),$$

$$\widetilde{f}_2(z,t) = -e^{-t} + ve^{-t}(0.5e^{0.5z} + 2\sin z\cos z)$$
$$-de^{-t}(0.25e^{0.5z} - 2\sin^2 z + 2\cos z)$$
$$-B_1 \exp\left(\frac{Ea_1}{R\ (298 + e^{-t}\sin^2 z)}\right) e^{-2t}(e^{0.5z} + \cos^2 z)(e^{0.5z} + \sin^2 z),$$

$$\widetilde{f}_3(z,t) = e^{t} + ve^{t}e^{z} - de^{t}e^{z}$$
$$+B_1 \exp\left(\frac{Ea_1}{R\ (298 + e^{-t}\sin^2 z)}\right) e^{-2t}(e^{0.5z} + \cos^2 z)(e^{0.5z} + \sin^2 z),$$

$$\widetilde{g}(z,t) = \left(\sum_{i=1}^{n} \mathcal{M}_i c_{v_i} y_i\right) v2\sin(z)\cos z - 2k(\sin^2 z - \cos^2 z)$$
$$+\Delta H(\theta) B_1 \exp\left(\frac{Ea_1}{R\ (298 + \sin^2 z)}\right)(e^{0.5z} + \cos^2 z)(e^{0.5z} + \sin^2 z).$$

We solve the problem in the time interval $[0, 1]$ and the space interval $[0, 1.5]$ for different step-sizes. The results are displayed in Table 6.3, for fixed spatial step corresponding to $N_z = 64$, and in Table 6.4, for fixed time step corresponding to $N_t = 64$. Notice that the error decreases in both cases and the order is at least two in time and in space.

N_t	L^2 error for species	L^2 error for temperature
4	0.0522535116589	0.001204334
8	0.0090397291651	0.000314024
16	0.0015456067776	5.78928E-05
32	0.0002422882547	8.10041E-06
64	0.0000307108686	9.6545066E-06

Table 6.3: Table of errors in L^2 norm

N_z	L^2 error for species	L^2 error for temperature
4	0.0097958014917	0.0029164006838
8	0.0090397291651	0.000314024
16	0.00059491811150000	0.00018666416840
32	0.000123880413800	0.000045250600800
64	0.0000307108686	0.0000096545066

Table 6.4: Table of errors in L^2 norm

Chapter 7

Numerical solution of the FBR model

In Chapter 3, we have described the general two-phase model for a heterogeneous fixed-bed reactor (FBR), including both species and temperature equations. These systems are more complex than PFR because one has to take into consideration the coupling between the fluid (macroscopic) and the solid (microscopic) phase models. Thus, the implementation of the FEM discretization and the coupling between phases is not easy to handle. For this reason, the implementation was done using the FeniCS library of finite elements `https://fenicsproject.org/` through a Python program. The FeniCS library allows us to write weak formulations of partial differential equations in an easy and direct way.

7.1 Weak formulation

In this section we build a weak formulation of the FBR model that will be used to define the numerical solution by means of finite element methods. Cylindrical coordinates are considered for the fluid phase and spherical coordinates for the solid phase. The main technical difficulty is the information transfer between the variables of the two phases, as they live in domains with different dimension (two for the fluid and three for the solid).

7.1.1 Macroscale: fluid bulk

Firstly, we consider the fluid bulk. Let us make the scalar product of equation (3.1) by a test function vector $\mathbf{u}(r, z)$ defined in $\Omega := (0, R) \times (0, L)$. Integrating in the whole reactor domain and using the cylindrical symmetry we get,

$$
\begin{aligned}
&2\pi \int_\Omega \frac{\partial}{\partial t}(\varepsilon^f \mathbf{y}^f)\cdot \mathbf{u} r\, dr\, dz + 2\pi \int_\Omega \frac{\partial}{\partial z}(\varepsilon^f v \mathbf{y}^f)\cdot \mathbf{u} r\, dr\, dz \\
&- 2\pi \int_\Omega \frac{1}{r}\frac{\partial}{\partial r}\Big(D_r^f r \frac{\partial}{\partial r}(\varepsilon^f \mathbf{y}^f)\Big)\cdot \mathbf{u} r\, dr\, dz - 2\pi \int_\Omega \frac{\partial}{\partial z}\Big(D_z^f r \frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f)\Big)\cdot \mathbf{u}\, dr\, dz \\
&= 2\pi \int_\Omega A^f \boldsymbol{\delta}^f(\theta^f, \mathbf{y}^f)\cdot \mathbf{u} r\, dr\, dz + 2\pi \int_\Omega \mathbf{g}\cdot \mathbf{u} r\, dr\, dz.
\end{aligned}
$$

Now we integrate by parts in the second, third and fourth terms on the left-hand side and we obtain,

$$
\begin{aligned}
&2\pi \int_\Omega \frac{\partial}{\partial t}(\varepsilon^f \mathbf{y}^f)\cdot \mathbf{u} r\, dr\, dz - 2\pi \int_\Omega \varepsilon^f v \mathbf{y}^f \cdot \frac{\partial \mathbf{u}}{\partial z} r\, dr\, dz \\
&- 2\pi \int_0^R \varepsilon^f(r,0) v \mathbf{y}^f(r,0)\cdot \mathbf{u}(r,0) r\, dr + 2\pi \int_0^R \varepsilon^f(r,L) v \mathbf{y}^f(r,L)\cdot \mathbf{u}(r,L) r\, dr \\
&+ 2\pi \int_\Omega D_r^f \frac{\partial}{\partial r}(\varepsilon^f \mathbf{y}^f)\cdot \frac{\partial \mathbf{u}}{\partial r} r\, dr\, dz + 2\pi \int_\Omega D_z^f \frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f)\cdot \frac{\partial \mathbf{u}}{\partial z} r\, dr\, dz \\
&- 2\pi \int_0^L D_r^f \frac{\partial}{\partial r}(\varepsilon^f \mathbf{y}^f)(R,z)\cdot \mathbf{u}(R,z) R\, dz + 2\pi \int_0^R D_z^f \frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f)(r,0)\cdot \mathbf{u}(r,0) r\, dr \\
&- 2\pi \int_0^R D_z^f \frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f)(r,L)\cdot \mathbf{u}(r,L) r\, dr \\
&= 2\pi \int_\Omega A^f \boldsymbol{\delta}^f(\theta^f, \mathbf{y}^f)\cdot \mathbf{u} r\, dr\, dz + 2\pi \int_\Omega \mathbf{g}\cdot \mathbf{u} r\, dr\, dz.
\end{aligned}
$$

By using the boundary conditions, this equality becomes,

$$
\begin{aligned}
&2\pi \int_\Omega \frac{\partial}{\partial t}(\varepsilon^f \mathbf{y}^f)\cdot \mathbf{u} r\, dr\, dz - 2\pi \int_\Omega \varepsilon^f v \mathbf{y}^f \cdot \frac{\partial \mathbf{u}}{\partial z} r\, dr\, dz \\
&+ 2\pi \int_0^R \varepsilon^f(r,L) v \mathbf{y}^f(r,L)\cdot \mathbf{u}(r,L) r\, dr \\
&+ 2\pi \int_\Omega D_r^f \frac{\partial}{\partial r}(\varepsilon^f \mathbf{y}^f)\cdot \frac{\partial \mathbf{u}}{\partial r} r\, dr\, dz + 2\pi \int_\Omega D_z^f \frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f)\cdot \frac{\partial \mathbf{u}}{\partial z} r\, dr\, dz \\
&= 2\pi \int_\Omega A^f \boldsymbol{\delta}^f(\theta^f, \mathbf{y}^f)\cdot \mathbf{u} r\, dr\, dz + 2\pi \int_\Omega \mathbf{g}\cdot \mathbf{u} r\, dr\, dz + 2\pi \int_0^R v \varepsilon^f \mathbf{y}_{in}^f(t)\cdot \mathbf{u} r\, dr.
\end{aligned} \tag{7.1}
$$

Now let us consider the energy equation. We multiply (3.8) by a scalar test function $u(r,z)$ defined in Ω. Integrating in the whole reactor domain and

using the cylindrical symmetry we get,

$$
\begin{aligned}
&2\pi \int_\Omega \varepsilon^f \rho^f \hat{c}_v^f(\theta^f) \frac{\partial \theta^f}{\partial t} u r \, dr \, dz + 2\pi \int_\Omega \varepsilon^f \rho^f \hat{c}_v^f(\theta^f) v \frac{\partial \theta^f}{\partial z} u r \, dr \, dz \\
&- 2\pi \int_\Omega \frac{1}{r} \frac{\partial}{\partial r} \Big(k_r^f r \frac{\partial \theta^f}{\partial r} \Big) u r \, dr \, dz - 2\pi \int_\Omega \frac{\partial}{\partial z} \Big(k_z^f \frac{\partial \theta^f}{\partial z} \Big) u r \, dr \, dz \\
&= 2\pi \int_\Omega f u r \, dr \, dz - 2\pi \int_\Omega \hat{\mathbf{w}}(\theta^f) \cdot \big(A^f \boldsymbol{\delta}^f(\theta^f, \mathbf{y}^f) + \mathbf{g} \big) u r \, dr \, dz.
\end{aligned}
$$

Integrating by parts the third and fourth terms on the left-hand side, we deduce

$$
\begin{aligned}
&2\pi \int_\Omega \varepsilon^f \rho^f \hat{c}_v^f(\theta^f) \frac{\partial \theta^f}{\partial t} u r \, dr \, dz + 2\pi \int_\Omega \varepsilon^f \rho^f \hat{c}_v^f(\theta^f) v \frac{\partial \theta^f}{\partial z} u r \, dr \, dz \\
&+ 2\pi \int_\Omega k_r^f \frac{\partial \theta^f}{\partial r} \frac{\partial u}{\partial r} r \, dr \, dz + 2\pi \int_\Omega k_z^f \frac{\partial \theta^f}{\partial z} \frac{\partial u}{\partial z} r \, dr \, dz + 2\pi \int_0^R k_r^f \frac{\partial \theta^f}{\partial r}(r, 0) u(r, 0) r \, dr \\
&- 2\pi \int_0^R k_r^f \frac{\partial \theta^f}{\partial r}(r, L) u(r, L) r \, dr + 2\pi \int_0^L k_z^f \frac{\partial \theta^f}{\partial z}(R, z) u(R, z) R \, dz \\
&= 2\pi \int_\Omega f u r \, dr \, dz - 2\pi \int_\Omega \hat{\mathbf{w}}(\theta^f) \cdot \big(A^f \boldsymbol{\delta}^f(\theta^f, \mathbf{y}^f) + \mathbf{g} \big) u r \, dr \, dz.
\end{aligned}
$$

Since we have a Dirichlet boundary condition at the reactor inlet (temperature is given at $z = 0$), we take the test function u null there. Using the boundary conditions at the reactor outlet and on the reactor wall the above equality becomes

$$
\begin{aligned}
&2\pi \int_\Omega \varepsilon^f \rho^f \hat{c}_v^f(\theta^f) \frac{\partial \theta^f}{\partial t} u r \, dr \, dz + 2\pi \int_\Omega \varepsilon^f \rho^f \hat{c}_v^f(\theta^f) v \frac{\partial \theta^f}{\partial z} u r \, dr \, dz \\
&+ 2\pi \int_\Omega k_r^f \frac{\partial \theta^f}{\partial r} \frac{\partial u}{\partial r} r \, dr \, dz + 2\pi \int_\Omega k_z^f \frac{\partial \theta^f}{\partial z} \frac{\partial u}{\partial z} r \, dr \, dz \\
&+ 2\pi \int_0^L h_{ext} \theta^f(R, z, t) u(R, z) R \, dz = 2\pi \int_\Omega f u r \, dr \, dz \\
&- 2\pi \int_\Omega \hat{\mathbf{w}}(\theta^f) \cdot \big(A^f \boldsymbol{\delta}^f(\theta^f, \mathbf{y}^f) + \mathbf{g} \big) u r \, dr \, dz + 2\pi \int_0^L h_{ext} \theta_{ext}(z, t) u(R, z) R \, dz.
\end{aligned}
$$

7.1.2 Micro-scale: spherical solid particles

Let us multiply equation (3.19) by a test function vector $\mathbf{u}(r_s, r, z)$, with $(r_s, r, z) \in (0, R_s) \times \Omega$. Integrating in the whole sphere and in the whole cylinder, and using spherical symmetry and cylindrical symmetry, respectively,

we get,

$$\begin{aligned}
&8\pi^2 \int_{(0,R_s)\times\Omega} \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial t} \cdot \mathbf{u} r_s^2 r \, dr_s \, dr \, dz \\
&- 8\pi^2 \int_{(0,R_s)\times\Omega} \frac{\partial}{\partial r_s}\Big(D^s r_s^2 \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial r_s}\Big) \cdot \mathbf{u} r \, dr_s \, dr \, dz \\
&= 8\pi^2 \int_{(0,R_s)\times\Omega} A^s \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s) \cdot \mathbf{u} r_s^2 r \, dr_s \, dr \, dz.
\end{aligned}$$

We integrate by parts the the second term of the left-hand side and we deduce that

$$\begin{aligned}
&8\pi^2 \int_{(0,R_s)\times\Omega} \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial t} \cdot \mathbf{u} r_s^2 r \, dr_s \, dr \, dz + 8\pi^2 \int_{(0,R_s)\times\Omega} D^s \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial r_s} \cdot \frac{\partial \mathbf{u}}{\partial r_s} r_s^2 r \, dr_s \, dr \, dz - \\
&\qquad 8\pi^2 \int_{\Omega} D^s \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial r_s} \cdot \mathbf{u} R_s^2 r \, dr \, dz = 8\pi^2 \int_{(0,R_s)\times\Omega} A^s \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s) \cdot \mathbf{u} r_s^2 r \, dr_s \, dr \, dz
\end{aligned}$$

and using the boundary conditions we get

$$\begin{aligned}
&8\pi^2 \int_{(0,R_s)\times\Omega} \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial t} \cdot \mathbf{u} r_s^2 \, dr_s r \, dr \, dz \\
&+ 8\pi^2 \int_{(0,R_s)\times\Omega} D^s \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial r_s} \cdot \frac{\partial \mathbf{u}}{\partial r_s} r_s^2 r \, dr_s \, dr \, dz \\
&+ 8\pi^2 \int_{\Omega} \eta_{fs}(r,z,t) \mathbf{y}^s(R^s, r, z, t) \cdot \mathbf{u}(R^s, r, z) R_s^2 r \, dr \, dz \qquad (7.2) \\
&= 8\pi^2 \int_{(0,R_s)\times\Omega} A^s \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s) \cdot \mathbf{u} r_s^2 r \, dr_s \, dr \, dz \\
&+ 8\pi^2 \int_{\Omega} \eta_{fs}(r,z,t) \mathbf{y}^f(r,z,t) \cdot \mathbf{u}(R^s, r, z) R_s^2 r \, dr \, dz.
\end{aligned}$$

Finally, if we make a change of variable defined by $x_s = \dfrac{r_s}{R_s}$, the weak formulation can be written as follows:

$$\begin{aligned}
&\int_{(0,1)\times\Omega} \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial t}(x^s, r, z, t) \cdot \mathbf{u}(x^s, r, z) R_s^3 x_s^2 \, dx_s r \, dr \, dz \\
&+ \int_{(0,1)\times\Omega} D^s \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial x_s}(x^s, r, z, t) \cdot \frac{\partial \mathbf{u}}{\partial x_s}(x^s, r, z) R_s x_s^2 r \, dx_s \, dr \, dz \\
&+ \int_{\Omega} \eta_{fs}(r,z,t) \mathbf{y}^s(1, r, z, t) \cdot \mathbf{u}(1, r, z) R_s^2 r \, dr \, dz \qquad (7.3) \\
&= \int_{(0,1)\times\Omega} A^s \boldsymbol{\delta}^s(\theta^s(x^s, r, z, t), \mathbf{y}^s(x^s, r, z, t)) \cdot \mathbf{u}(x^s, r, z) R_s^3 x_s^2 r \, dx_s \, dr \, dz \\
&+ \int_{\Omega} \eta_{fs}(r,z,t) \mathbf{y}^f(r,z,t) \cdot \mathbf{u}(1, r, z) R_s^2 r \, dr \, dz.
\end{aligned}$$

Now let us consider the energy equation. We multiply equation (3.22) by a test function $u(r_s, r, z)$, with $(r_s, r, z) \in (0, R_s) \times \Omega$. Integrating in the whole sphere and in the whole cylinder, and using spherical symmetry and cylindrical symmetry, respectively, we get

$$\begin{aligned}
&8\pi^2 \int_{(0,R_s)\times\Omega} \varepsilon^s \rho^s \hat{c}_v^s(\theta^s) \frac{\partial \theta^s}{\partial t} u r_s^2 r \, dr_s \, dr \, dz \\
&- 8\pi^2 \int_{(0,R_s)\times\Omega} \frac{1}{r_s^2} \frac{\partial}{\partial r_s} \Big(k^s r_s^2 \frac{\partial \theta^s}{\partial r_s} \Big) u r_s^2 r \, dr_s \, dr \, dz \\
&= -8\pi^2 \int_{(0,R_s)\times\Omega} \hat{\mathbf{w}}(\theta^s) \cdot A^s \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s) u r_s^2 r \, dr_s \, dr \, dz.
\end{aligned}$$

Integrating by parts in the second term of the left-hand side we deduce that

$$\begin{aligned}
&8\pi^2 \int_{(0,R_s)\times\Omega} \varepsilon^s \rho^s \hat{c}_v^s(\theta^s) \frac{\partial \theta^s}{\partial t} u r_s^2 r \, dr_s \, dr \, dz \\
&+ 8\pi^2 \int_{(0,R_s)\times\Omega} k^s \frac{\partial \theta^s}{\partial r_s} \frac{\partial u}{\partial r_s} r_s^2 r \, dr_s \, dr \, dz \\
&- 8\pi^2 \int_{\Omega} k^s \frac{\partial \theta^s}{\partial r_s}(R_s, r, z, t) u(R_s, r, z) R_s^2 r \, dr_s \, dr \, dz \\
&= -8\pi^2 \int_{(0,R_s)\times\Omega} \hat{\mathbf{w}}(\theta^s) \cdot A^s \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s) u r_s^2 r \, dr \, dz,
\end{aligned}$$

and using the boundary conditions, we obtain the weak formulation for the energy equation in the micro-scale model:

$$\begin{aligned}
&8\pi^2 \int_{(0,R_s)\times\Omega} \varepsilon^s \rho^s \hat{c}_v^s(\theta^s) \frac{\partial \theta^s}{\partial t} u r_s^2 r \, dr_s \, dr \, dz \\
&+ 8\pi^2 \int_{(0,R_s)\times\Omega} k^s r_s^2 \frac{\partial \theta^s}{\partial r_s} \frac{\partial u}{\partial r_s} r \, dr_s \, dr \, dz \\
&+ 8\pi^2 \int_{\Omega} h_{fs}(r, z, t) \theta^s(R^s, r, z, t) u(R_s, r, z) R_s^2 r \, dr \, dz \\
&= -8\pi^2 \int_{(0,R_s)\times\Omega} \hat{\mathbf{w}}(\theta^s) \cdot A^s \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s) u r_s^2 r \, dr_s \, dr \, dz \\
&+ 8\pi^2 \int_{\Omega} h_{fs}(r, z, t) \theta^f(r, z, t) u(R_s, r, z) R_s^2 r \, dr \, dz.
\end{aligned}$$

Finally, we introduce the change of variable $x_s = \dfrac{r_s}{R_s}$:

$$
\begin{aligned}
&\int_{(0,1)\times\Omega} \varepsilon^s \rho^s \hat{c}_v^s(\theta^s(x^s,r,z,t)) \frac{\partial \theta^s}{\partial t}(x^s,r,z,t) u(x^s,r,z) R_s^3 r \, dx_s \, dr \, dz \\
&+ \int_{(0,1)\times\Omega} k^s R_s \frac{\partial \theta^s}{\partial x_s}(x^s,r,z,t) \frac{\partial u}{\partial x_s}(x^s,r,z) r \, dx_s \, dr \, dz \\
&+ \int_{\Omega} h_{fs}(r,z,t) \theta^s(1,r,z,t) u(1,r,z) R_s^2 r \, dr \, dz \\
&= - \int_{(0,1)\times\Omega} \hat{\mathbf{w}}(\theta^s(x^s,r,z,t)) \cdot A^s \boldsymbol{\delta}^s(\theta^s(x^s,r,z,t), \mathbf{y}^s(x^s,r,z,t)) u(x^s,r,z) R_s^3 r \, dx_s \, dr \, dz \\
&+ \int_{\Omega} h_{fs}(r,z,t) \theta^f(r,z,t) u(1,r,z) R_s^2 r \, dr \, dz.
\end{aligned}
$$

7.1.3 Mass conservation at steady-state

In this paragraph we obtain a mass conservation equation for the whole multi-scale model at steady-state. Hence, all fields are time independent, thus the accumulation terms are null in all equations.

Let us start by using the micro-scale model and take the test function

$$\mathbf{u}(r,z) = \frac{a(r,z)}{R_s^2(r,z)} \boldsymbol{\mathcal{M}}$$

in (7.2), where a is given by (3.31). As the partial derivative of this function with respect to r_s is null, we obtain

$$
\begin{aligned}
&8\pi^2 \int_{\Omega} \frac{a}{R_s^2} \eta_{fs}(r,z) \mathbf{y}^s(R^s,r,z) \cdot \boldsymbol{\mathcal{M}} R_s^2 r \, dr \, dz \\
&= 8\pi^2 \int_{(0,R_s)\times\Omega} \frac{a}{R_s^2} A^s \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s) \cdot \boldsymbol{\mathcal{M}} r_s^2 r \, dr_s \, dr \, dz \\
&+ 8\pi^2 \int_{\Omega} \frac{a}{R_s^2} \eta_{fs}(r,z) \mathbf{y}^f(r,z) \cdot \boldsymbol{\mathcal{M}} R_s^2 r \, dr \, dz \\
&= 8\pi^2 \int_{(0,R_s)\times\Omega} \frac{a}{R_s^2} \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s) \cdot (A^s)^t \boldsymbol{\mathcal{M}} r_s^2 r \, dr_s \, dr \, dz \\
&+ 8\pi^2 \int_{\Omega} \frac{a}{R_s^2} \eta_{fs}(r,z) \mathbf{y}^f(r,z) \cdot \boldsymbol{\mathcal{M}} R_s^2 r \, dr \, dz \\
&= 8\pi^2 \int_{\Omega} \frac{a}{R_s^2} \eta_{fs}(r,z) \mathbf{y}^f(r,z) \cdot \boldsymbol{\mathcal{M}} R_s^2 r \, dr \, dz,
\end{aligned}
$$

because $(A^s)^t\boldsymbol{\mathcal{M}} = 0$ (see (1.2)). Therefore,

$$\begin{aligned} &8\pi^2 \int_\Omega a(r,z)\eta_{fs}(r,z)\mathbf{y}^s(R^s(r,z),r,z)\cdot\boldsymbol{\mathcal{M}} r\,dr\,dz \\ &= 8\pi^2 \int_\Omega a(r,z)\eta_{fs}(r,z)\mathbf{y}^f(r,z)\cdot\boldsymbol{\mathcal{M}} r\,dr\,dz. \end{aligned} \tag{7.4}$$

Now, let us consider the bulk fluid. We take the test function $\mathbf{u} = \boldsymbol{\mathcal{M}}$ in the weak formulation (7.1) and we get

$$\begin{aligned} &2\pi \int_0^R v\varepsilon^f(r,L)\mathbf{y}^f(r,L)\cdot\boldsymbol{\mathcal{M}} r\,dr = 2\pi \int_\Omega A^f\boldsymbol{\delta}^f(\theta^f,\mathbf{y}^f)\cdot\boldsymbol{\mathcal{M}} r\,dr\,dz \\ &+ 2\pi \int_\Omega \mathbf{g}\cdot\boldsymbol{\mathcal{M}} r\,dr\,dz + 2\pi\int_0^R \mathbf{c}^f_{in}\cdot\boldsymbol{\mathcal{M}} r\,dr \\ &= 2\pi \int_\Omega \boldsymbol{\delta}^f(\theta^f,\mathbf{y}^f)\cdot(A^f)^t\boldsymbol{\mathcal{M}} r\,dr\,dz + 2\pi\int_\Omega \mathbf{g}\cdot\boldsymbol{\mathcal{M}} r\,dr\,dz \\ &+ 2\pi\int_0^R v\varepsilon^f(r,0)\mathbf{y}^f_{in}\cdot\boldsymbol{\mathcal{M}} r\,dr = 2\pi\int_\Omega \mathbf{g}\cdot\boldsymbol{\mathcal{M}} r\,dr\,dz + 2\pi\int_0^R v\varepsilon^f(r,0)\mathbf{y}^f_{in}\cdot\boldsymbol{\mathcal{M}} r\,dr, \end{aligned} \tag{7.5}$$

again, because $(A^f)^t\boldsymbol{\mathcal{M}} = 0$ (see (1.2)).

In the following we prove that $\displaystyle\int_\Omega \mathbf{g}\cdot\boldsymbol{\mathcal{M}} r\,dr\,dz = 0$. Indeed, from the definition of $\mathbf{g}$ (see (3.33)) and by using (7.4) we have,

$$\int_\Omega \mathbf{g}\cdot\boldsymbol{\mathcal{M}} r\,dr\,dz = \int_\Omega a(r,z)\eta_{fs}(r,z)\Big(\mathbf{y}^s\big(R^s(r,z),r,z\big) - \mathbf{y}^f(r,z)\Big)\cdot\boldsymbol{\mathcal{M}} r\,dr\,dz = 0.$$

Then (7.5) yields

$$2\pi\int_0^R v\varepsilon^f(r,L)\mathbf{y}^f(r,L)\cdot\boldsymbol{\mathcal{M}} r\,dr = 2\pi\int_0^R v\varepsilon^f(r,0)\mathbf{y}^f_{in}\cdot\boldsymbol{\mathcal{M}} r\,dr.$$

The left-hand side is the total mass flow rate (kg/s) leaving the reactor, while the right-hand side is the total mass flow rate (kg/s) entering the reactor. Therefore, we have proved that the model conserves the total mass.

7.2 An academic test in steady state

In order to validate the finite element implementation we consider an academic example for a steady FBR with resistance. We recall that using the notation from Chapter 3 the full model is the following:

$$
\begin{aligned}
\frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f v) - \frac{1}{r}\frac{\partial}{\partial r}\Big(D_r^f r \frac{\partial}{\partial r}(\varepsilon^f \mathbf{y}^f)\Big) - \frac{\partial}{\partial z}\Big(D_z^f \frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f)\Big) \\
= A^f \boldsymbol{\delta}^f(\theta^f, \mathbf{y}^f) + a\eta_{fs}\big(\mathbf{y}^s(R^s) - \mathbf{y}^f\big), \\
\varepsilon^f \rho^f \hat{c}_v^f(\theta^f) v \frac{\partial \theta^f}{\partial z} - \frac{1}{r}\frac{\partial}{\partial r}\Big(k_r^f r \frac{\partial \theta^f}{\partial r}\Big) - \frac{\partial}{\partial z}\Big(k_z^f \frac{\partial \theta^f}{\partial z}\Big) \\
= a h_{fs}\big(\theta^s(R^s) - \theta^f\big) - \hat{\mathbf{w}}(\theta^f) \cdot A^f \boldsymbol{\delta}^f(\theta^f, \mathbf{y}^f), \\
\\
-\frac{1}{r_s^2}\frac{\partial}{\partial r_s}\Big(D^s r_s^2 \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial r_s}\Big) = A^s \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s), \\
-\frac{1}{r_s^2}\frac{\partial}{\partial r_s}\Big(k^s r_s^2 \frac{\partial \theta^s}{\partial r_s}\Big) = -\hat{\mathbf{w}}(\theta^s) \cdot A^s \boldsymbol{\delta}^s(\theta^s, \mathbf{y}^s), \\
\\
-D_z^f \frac{\partial}{\partial z}(\varepsilon^f \mathbf{y}^f)(r,0) + v\varepsilon^f \mathbf{y}^f(r,0) = v\varepsilon^f \mathbf{y}_{in}^f, \\
\theta^f(r,0) = \theta_{in}^f, \\
\frac{\partial \varepsilon^f \mathbf{y}^f}{\partial z}(r,L) = \mathbf{0}, \\
\frac{\partial \theta^f}{\partial z}(r,L) = 0, \\
\frac{\partial \varepsilon^f \mathbf{y}^f}{\partial r}(R,z) = \mathbf{0}, \\
k_r^f \frac{\partial \theta^f}{\partial r}(R,z) = h_{ext}\big(\theta_{ext}(t) - \theta^f(R,z)\big), \\
\frac{\partial \varepsilon^f \mathbf{y}^f}{\partial r}(0,z) = \mathbf{0}, \\
\frac{\partial \theta^f}{\partial r}(0,z) = 0, \\
\frac{\partial (\varepsilon^s \mathbf{y}^s)}{\partial r_s}(0,r,z) = \mathbf{0}, \\
\frac{\partial \theta^s}{\partial r_s}(0,r,z) = 0, \\
D^s \frac{\partial \varepsilon^s \mathbf{y}^s}{\partial r_s}(R^s(r,z),r,z) = \eta_{fs}(r,z)\Big(\mathbf{y}^f(r,z) - \mathbf{y}^s(R^s(r,z),r,z)\Big), \\
k^s \frac{\partial \theta^s}{\partial r_s}(R^s(r,z),r,z) = h_{fs}(r,z)\big(\theta^f(r,z) - \theta^s(R^s(r,z),r,z)\big).
\end{aligned}
$$

We define a stationary problem with known analytical solution. The reaction system is described by 4 species involved in 2 reactions in the fluid phase whose kinetic is governed by law of mass action:

$$\begin{aligned} S_1^f + S_2^f \to S_3^f \qquad &\longrightarrow \qquad \delta_1^f(\theta^f, \mathbf{y}^f) = B_1 e^{\left(-\frac{Ea_1}{R\theta^f}\right)} y_1^f y_2^f \\ S_1^f + S_3^f \to S_4^f \qquad &\qquad\quad\ \ \delta_2^f(\theta^f, \mathbf{y}^f) = B_2 e^{\left(-\frac{Ea_2}{R\theta^f}\right)} y_1^f y_3^f, \end{aligned}$$

with coefficients $B_1 = 1.0\ 10^{10}$, $Ea_1 = 7.5\ 10^4$, $B_2 = 1.0\ 10^8$ and $Ea_2 = 9.0\ 10^4$.

We assume that the reaction system is the same at the microscale level, that is, inside the solid particles.

Now we define the solution:

$$\begin{aligned} \hat{y}_1^s(x_s, r, z, t) &= \cos^2 z + r^2 + x_s^2, \\ \hat{y}_2^s(x_s, r, z, t) &= \sin^2 z + r^3 + x_s^3, \\ \hat{y}_3^s(x_s, r, z, t) &= \sin^2 z + \cos^2 r + x_s^4, \\ \hat{y}_4^s(x_s, r, z, t) &= \cos^2 z + \sin^2 r + x_s^5, \\ \hat{\theta}^s(x_s, r, z, t) &= 2z^2 + r^2 + x_s + 280, \end{aligned} \tag{7.6}$$

$$\begin{aligned} \hat{y}_1^f(r, z, t) &= 2\frac{\varepsilon^s D_1^s}{\eta_{fs} R^s} + \cos^2 z + r^2 + 1, \\ \hat{y}_2^f(r, z, t) &= 3\frac{\varepsilon^s D_2^s}{\eta_{fs} R^s} + \sin^2 z + r^3 + 1, \\ \hat{y}_3^f(r, z, t) &= 4\frac{\varepsilon^s D_3^s}{\eta_{fs} R^s} + \sin^2 z + \cos^2 r + 1, \\ \hat{y}_4^f(r, z, t) &= 5\frac{\varepsilon^s D_4^s}{\eta_{fs} R^s} + \cos^2 z + \sin^2 r + 1, \\ \hat{\theta}^f(r, z, t) &= \frac{\varepsilon^s k^s}{h_{fs} R^s} + 2z^2 + r^2 + 281. \end{aligned} \tag{7.7}$$

These functions are a solution of the above system of equations by adding an auxiliary *source* function at each equation, namely,

$$
\begin{aligned}
f^f_{aux_i} &= \frac{\partial}{\partial z}(\varepsilon^f \hat{y}^f_i v) - \frac{1}{r}\frac{\partial}{\partial r}\Big(D^f_r r \frac{\partial}{\partial r}(\varepsilon^f \hat{y}^f_i)\Big) - \frac{\partial}{\partial z}\Big(D^f_z \frac{\partial}{\partial z}(\varepsilon^f \hat{y}^f_i)\Big) \\
&\quad - A^f \hat{\boldsymbol{\delta}}^f - a\eta_{fs}\big(\hat{y}^s_i(1) - \hat{y}^f_i\big), \\
g^f_{aux} &= \varepsilon^f \rho^f \hat{c}^f_v(\hat{\theta}^f) v \frac{\partial \hat{\theta}^f}{\partial z} - \frac{1}{r}\frac{\partial}{\partial r}\Big(k^f_r r \frac{\partial \hat{\theta}^f}{\partial r}\Big) - \frac{\partial}{\partial z}\Big(k^f_z \frac{\partial \hat{\theta}^f}{\partial z}\Big) \\
&\quad + \hat{\mathbf{w}}(\hat{\theta}^f)\cdot A^f \hat{\boldsymbol{\delta}}^f - ah_{fs}\big(\hat{\theta}^s(1) - \hat{\theta}^f\big), \\
f^s_{aux_i} &= \frac{\partial}{\partial t}(\varepsilon^s \hat{y}^s_i) - \frac{1}{r_s^2}\frac{\partial}{\partial r_s}\Big(D^s r_s^2 \frac{\partial \varepsilon^s \hat{y}^s_i}{\partial r_s}\Big) - A^s \hat{\boldsymbol{\delta}}^s, \\
g^s_{aux} &= -\frac{1}{r_s^2}\frac{\partial}{\partial r_s}\Big(k^s r_s^2 \frac{\partial \hat{\theta}^s}{\partial r_s}\Big) - \hat{\mathbf{w}}(\theta^s)\cdot A^s \hat{\boldsymbol{\delta}}^s, \quad i = 1, ..., N,
\end{aligned}
$$

where $\hat{\boldsymbol{\delta}}^s = \boldsymbol{\delta}^f(\hat{\theta}^f, \hat{\mathbf{y}}^f)$ and $\hat{\boldsymbol{\delta}}^s = \boldsymbol{\delta}^f(\hat{\theta}^s, \hat{\mathbf{y}}^s)$.

We also need to modify the homogeneous Neumann boundary conditions at the reactor inlet and replace them by Robin boundary conditions.

The coefficients appearing in the model are summarized in the following tables:

Species coefficients	S_1	S_2	S_3	S_4
Molecular weigths ($\mathcal{M}$)	42	138	122	58
Specific heat ($\hat{c}^f_v$)	2000	2000	2000	2000
Radial diffusions in macro scale (D^f_r)	1.0e-1	1.0e-1	1.0e-1	1.0e-1
Axial diffusions in macro scale (D^f_z)	1.0e+1	1.0e+1	1.0e+1	1.0e+1
Mass diffusion in micro scale (D^s)	1.0e-10	1.0e-10	1.0e-10	1.0e-10

Table 7.1: Coefficients of chemical species

Reaction measurements	T^a formation	Reac 1	Reac 2
Heat of form. in macro scale ($\Delta\hat{H}^f(\theta^*)$)	298.15	1.0e+08	8.0e+07
Heat of form. in micro scale ($\Delta\hat{H}^s(\theta^*)$)	298.15	1.0e+08	8.0e+07

Table 7.2: Heats of formation in macro and micro scales

Effective, transfer and porosity coefficients	
Energy coefficient in macro scale: radial and axial (k_r^f and k_z^f)	1.0e-07
Energy coefficient in micro scale (k^s)	1.0e-07
Transfer fluid-solid coefficient for species (η_{fs})	3.38e-7
Transfer fluid-solid coefficient for temperature (h_{fs})	1.0e-5
Overall heat transfer coefficient (h_{ext})	30.0
Bulk porosity (ε^f)	0.45
Solid porosity (ε^s)	0.4

Table 7.3: Transference, effectiveness and porosity coefficients

In this example the radius of the reactor is 0.01 m, its length is 1.0 m and the expression of the particles radius is $R^s(r, z, t) = 0.004$ m.

The academic test we present has been computed using Batea which is an interface over FEniCS that resolves the full model with unknowns that live in different domains. Numerical versus analytical solution can be observed in the following graphs for the most refined mesh:

a) Analytical solution of y_4^f **b)** Numerical solution of y_4^f

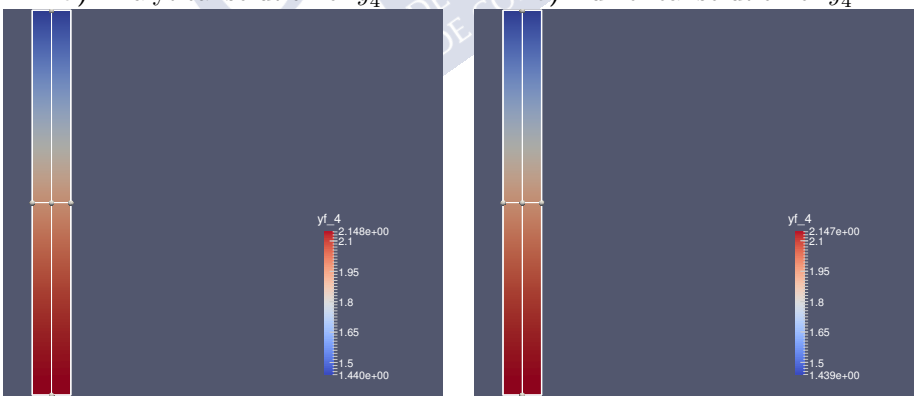

Figure 7.1: Analytical vs Numerical concentrations in the macro-scale

a) Analytical solution of y_2^s **b)** Numerical solution of y_2^s

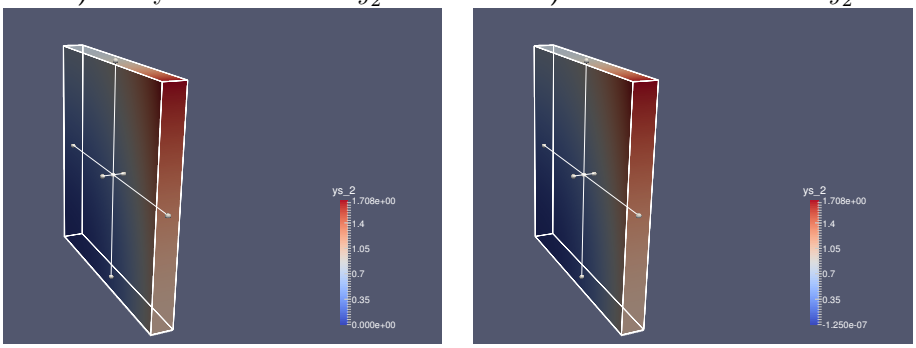

Figure 7.2: Analytical vs Numerical concentrations

Notice that the profile of numerical and analytical solutions is the same. We observe a little difference in lower values of solution near zero.

To perform the error and order of accuracy analysis we employ three uniform meshes with different cell sizes, both for micro and macro scales, described in Table 7.4 and Table 7.5.

Mesh	n_r	n_z	Elements-triangles
M_1^f	15	5	112
M_2^f	30	10	2412
M_3^f	60	20	10412

Table 7.4: Macro scale mesh features

Mesh	n_r	n_z	n_{x_s}	Elements-tetrahedra
M_1^s	15	5	5	1344
M_2^s	30	10	10	14094
M_3^s	60	20	20	127794

Table 7.5: Micro scale mesh features

Finally, we present the error table for the different meshes when using continuous piecewise linear finite elements.

	Error in $L^2(\Omega)$ norm			Order of the method	
	M_1^f	M_2^f	M_3^f	$O_{M_1^f/M_2^f}$	$O_{M_2^f/M_3^f}$
$\mathbf{y}^f$	5.31040e-03	1.04863E-03	2.37881e-04	2.34030924	2.14020096
$\boldsymbol{\theta}^f$	2.63086e-03	4.99771e-04	9.34071e-05	2.39619717	2.41966297
	M_1^s	M_2^s	M_3^s	$O_{M_1^s/M_2^s}$	$O_{M_2^s/M_3^s}$
$\mathbf{y}^s$	5.77722e-03	1.16707e-03	2.62987e-04	2.30748936	2.14982345
$\boldsymbol{\theta}^s$	2.28600e-03	4.55834e-04	1.12632e-04	2.32624447	2.01688713

Table 7.6: Observed errors and convergence orders

The order has been computed as

$$O_{M_i/M_j} = \frac{\log(e_{M_i}/e_{M_j})}{\log(h_{M_i}/h_{M_j})}$$

and

$$e_{M_i} = \left(\int_\Omega ||\mathbf{y}^f - \hat{\mathbf{y}}^f||^2 dx \right)^{\frac{1}{2}}$$

represents the error in the $\mathbf{L}^2(\Omega)$ norm in M_i^f and M_i^s meshes for the number of elements specified in Table 7.4 and Table 7.5, respectively.

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Conclusions

Through this Part II we have proved a global existence theorem for convection-diffusion-reaction systems. The property of boundedness of total mass needed for the global existence cannot be repeated for the energy equation. Then, we have proved the theorem only for the species system. We have followed the variational approach combined with semigroup theory. The proof of this theorem is based on techniques presented in details in [55]. Thus, we explore properties **(P)** and **(M)** that were verified because of the form of our particular reaction term (the law of mass action), and because the variables in our problem represent chemical species and so the positivity of their concentrations is a natural property.

We have proposed a space semidiscretization for which an existence theorem is proved and error estimates are also given.

Finally, we obtained the numerical solution of the models that interest us from the practical point of view: PFR and FBR models. For the first one we have used a finite difference scheme, while for the FBR model a finite element method was proposed. The implementation was validated using an academic case of FBR in steady state with resistance.

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Part III

Identification in reaction systems

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Introduction

Reaction systems are widely used for controlling, monitoring and optimizing industrial processes. Their study makes extensive employment of mathematical modelling in terms of differential equations expressing the conservation of mass and energy in order to describe concentrations, volume or temperature. Building these models needs the identification of the reactions taking place and their corresponding kinetics. One of the most challenging task is the identification of the kinetic laws: the identification of the best kinetic model from a list of proposed functional forms and also finding the optimal values of their corresponding parameters. The main difficulties appear in the *a priori* statement of the shape of the kinetics and in the amount of degrees of freedom in the optimization problem. The first one requires the help and the experience of an expert in order to define the general expression of the functions with the parameters to be identified. The second one is related to overfitting. This can be avoided using adequate optimization techniques and including as parameters susceptible to optimize those that the expert considers necessary.

In this part we present a methodology for solving the inverse problem described above, also called model identification problem. We are interested in identifying kinetic models and their corresponding parameters, using a set of experimental data and the reactions taking place. The identification can be done in one step via an integral approach or sequential via an incremental approach [12]. This method decomposes the initial identification problem in sub-problems in which each reaction can be determined individually [5, 18]. In the following sections we describe a methodology introduced in [7] that consists in the combination of two methods: incremental and integral. This approach is illustrated with examples of stirred tank reactors described in details in Chapter 1.

There are situations when not all the species are measurable, or species information is missing in some time instants. In these cases, the methodology from [7] for solving inverse identification problems sometimes does not produce good results. Thus, the identification problem to solve is replaced by the problem of inferring parameters in chemical reactions networks where the available

information, either in transient or steady state, has missing concentration values. In some cases, the available data is enough to recover the parameters in the kinetics and thus "the system is identifiable" [17]. In other cases, the methodology provides a range of the missing concentrations of species using extreme (highest and lowest) concentrations under incomplete data measurements. The model parameters associated with such extreme concentrations are obtained [13].

Another challenging problem in this field is the so called model selection that consists in determining the experimental initial values in the ODEs system which allow us to discriminate among several models. A way of model selection in chemical reaction network is done using global optimization method, as described in detail in [14].

Identification problem regards different approaches, apart of kinetics identification. See for example the work of Burnham and Willis [21] in which they identify chemical reaction networks assuming no *a priori* information about reaction stoichiometries or species structures, through the analysis of process data obtained in a laboratory environment. Another approach is described in [64]. In this article the stoichiometry and kinetic model are selected using two consecutive optimization steps using integer linear programming. The first one consists onobtaining a list of all feasible stoichiometric relations is developed and the second one uses these relations to construct all plausible combinations of the stoichiometric equations which are used to instantiate kinetic model structures.

Chapter 8

The identification problem in reaction systems

In order to solve our identification problem, we apply two approaches in cascade: incremental and integral methods [7]. The use of these two methods in cascade can be replicated for some of the most typical reactors, such as stirred tank reactors (batch, semi batch or continuous) and plug flow reactors, both extensively used in literature and industry. Such identification processes are usually studied in systems where the phenomena of interest can be observed in isolation, without other physical phenomena interference. It is the case of reaction kinetics in liquid phase, where a stirred batch or semi batch reactor is used in the majority of cases [17]. Of course, an important aspect to be taken into account is the set of measurements obtained in laboratory that will be included in the parameters adjustment of these kinetics.

In this chapter, we focus on the identification of kinetic models on stirred tank reactors, using a set of experimental data and the reactions taking place. A catalogue of kinetic models containing the parameters to be identified will be provided too.

It is important to mention that the incremental method described in Section 8.4.1 can be applied only to STR and PFR reactors. However, the integral method can be used even for FBR model.

8.1 Measurements and reactions scheme

Experimental data is required in the optimization process for the adjustment of the parameters characterizing the kinetic model. These measurements are species concentration, temperature, inlet/outlet flow rates, among others. In addition, physico-chemical parameters of the species such as molecular weight

($kg/kmol$), specific heat (J/kgK) and reaction heat ($J/kmol$) at formation temperature (usually 298.15 K) are also needed.

In the case of the batch reactor we consider in the following, measurements are related to the concentration of chemical species, volume of the mixture and also mixture temperature at some time instants. All these data are collected in several experiments under different conditions.

8.2 Kinetic models

An important step in the identification process is a good definition of a kinetic catalogue. The specification must take into account the chemical knowledge and the experience of an expert for defining reaction rates susceptible to be selected. It is important to consider the most relevant parameters to avoid overfitting.

In practice it is possible to write "ad hoc" kinetics to define any functional form in the identification, but the integral method works better with general expressions known *a priori* because it is very useful for computing the gradient of the functional cost by means of adjoint method. This is explained in details in Section 8.4.2.

The general expression of the reaction rates we use is given by:

$$\delta_r(\theta, \mathbf{y}, \mathbf{z}) = B_r exp\left(-\frac{E_{a_r}}{\mathcal{R}\theta}\right) \prod_{j=1}^{M_r} \left(\sum_{m=1}^{P_j^r} G_{j,m}^r \prod_{n=1}^{N} y_n^{\beta_{j,m,n}^r} \prod_{n=1}^{N_c} z_n^{\beta_{j,m,n+N}^r} + b_j^r \right)^{\alpha_j^r}$$

with $1 \leq r \leq L$.

The first part corresponds to the Arrhenius law, described in Section 1.1.3. Two parameters, the pre-exponential (or frequency) factor (B_r) and the activation energy (E_a^r) must be adjusted. Notice that if B_r tends to zero, the corresponding reaction term can be neglected. The second part is formed by powers of combinations of powers of concentrations. In this case, divisions by zero may appear because negative exponents are allowed.

During computational tests we have used the following common bounds for the above mentioned parameters:

- $B_r \in [0, 10^{14}]$,
- $E_a^r \in [0, 2.0 \times 10^5]$,
- $G_{j,m}^r \in [0, 1]$,
- $\beta_{j,m,n}^r \in [0, 2]$,

- $b_j^r \in [0, 100]$
- $\alpha_j^r \in [-2, 2]$.

8.3 The general model

As we explained at the beginning of this chapter, we focus on an important family of chemical reactors: the so-called stirred tank reactors (STR). We assume that the mixture inside these reactors is homogeneous because of stirring, thus the physico-chemical magnitudes do not depend on position. Hence, they are modelled as (usually stiff) coupled, non-linear ordinary differential equations.

We consider a model involving mass and heat balance equations. In addition, we have an equation for volume variation, but this equation is decoupled from the rest. In the experimental environment, additional variables appear in the model. They are the catalysts, which help the reactions to occur or to make the process faster, but in our model they are not considered. The model is written in general form as

$$\begin{cases} \dfrac{d\mathbf{y}}{dt} = \mathbf{f}(\theta, \mathbf{y}, \mathbf{z}) \text{ in } [0, T], & \text{mass balance euqations} \\ \dfrac{d\theta}{dt} = h(\theta, \mathbf{y}, \mathbf{z}), & \text{heat balance equation} \\ \dfrac{dV}{dt} = \mathrm{f}^2 - \mathrm{f}^3, & \text{volume equation} \\ \mathbf{y}(0) = \mathbf{y}_0, \theta(0) = \theta_0 \text{ and } V(0) = V_0, \end{cases} \tag{8.1}$$

with the source terms

$$\mathbf{f} = A\boldsymbol{\delta}(\theta, \mathbf{y}, \mathbf{z}) + \frac{1}{V}(\mathrm{F}\mathbf{f}^1 - \mathrm{f}^2\mathbf{y}),$$

$$h = \frac{\boldsymbol{\Delta}\mathbf{H}(\theta) \cdot \boldsymbol{\delta}(\theta, \mathbf{y}, \mathbf{z}) - \dfrac{g}{V}(\theta_{out} - \theta) - \mathbf{w}'(\theta) \cdot \left(\mathrm{F} \displaystyle\sum_{p=1}^{P} \mathrm{f}_p^1 (\theta_p^s - \theta)\mathbf{e}_p \right)}{\mathbf{w}'(\theta) \cdot \mathbf{y}},$$

with

$$\boldsymbol{\Delta}\mathbf{H}(\theta) = A^t \mathbf{w}(\theta),\ w_i(\theta) = \mathcal{M}_i e_i \text{ and } e_i(\theta) = e_i^* + \int_{\theta^*}^{\theta} c_i(s)ds \text{ for the}$$

$i - th$ species

and

$\mathbf{y}$ represents the vector of species concentrations,

θ represents the temperature of mixture,

$\mathbf{z}$ represents the vector of catalysts,

V represents the volume of the mixture,

A is the stoichiometric matrix,

$\boldsymbol{\delta}$ represents the vector of reaction velocities,

F represents the inlet composition,

$\mathbf{f}_1$ is the vector of inlet flow rates,

f_2 is the sum of components in $\mathbf{f}_1$, that is the outlet flow,

f_3 is the outlet flow rate,

$\mathbf{\Delta H}$ is the vector of heat of reactions,

g is a heat transfer coefficient,

θ_{out} is the outside temperature,

θ_p^s is the temperature of the p-th stream, where P is the number of streams,

$\mathcal{M}_i$ is the molecular mass of the i-th species,

c_i is the specific heat of the i-th species,

e_i is the internal energy of the i-th specie,

e_i^* is the internal energy of formation of the i-th species at temperature θ^*.

In general, we have continuous inlet and outlet streams. In this case, the reactor is called ***continuous STR***. If we have only inlet streams the reactor is called ***semi-batch STR***, and if no inlet or outlet streams are considered, the reactor is called ***batch STR***.

8.4 Model selection and parameter identification

For an optimal identification process, a suitable model is desired including information of stoichiometry matrix and a "good" expression for the rate of reactions. The model can be solved by considering several techniques such as differential, integral or incremental methods [12], employing experimental data.

Of course, all they can be used independently or we can combine some of them to obtain more accurate solutions.

Differential method uses cubic spline functions interpolating the data and trying to minimize the residual of the differential equations system taking their derivatives at time measurements. The error in these derivatives may affect the accuracy of the results.

In this chapter we focus on incremental and integral methods. The incremental method works with the concept of "extent", which provides an analytic solution of an equivalent decoupled system. The second one needs to solve numerically the initial ODEs model. Then, the unknown parameters are determined comparing experimental data with model predictions. In some cases, if the solution obtained using the incremental method is good enough we can conclude the identification process, but this is not always true and thus the integral method is needed to improve the solution using the initial solution provided by the incremental method.

8.4.1 Initial approximation: The incremental method.

The incremental approach is characterized by the fact that each rate process is modeled individually, independently of the other rate processes, thus the identification problem is decomposed into a set of subproblems, one for each kinetic. The incremental technique is firstly introduced, although of differential type, as the reactions and inlet-outlet flows are obtained by differentiation of measured concentrations, for Batch STR reactors in [5] and for CSTR reactors in [18] (only for mole balance equation in both articles). These references led to a relatively recent concept, called ***extent***. Its definition appears in [2] where a linear transformation that computes the extents of reaction from the numbers of moles in homogeneous reaction systems with inlet and outlet streams is proposed. It is extended in [10] for gas-liquid reaction systems. After that, it has been studied for the STR model with mole and heat balance equations in [12] and for PFR model in [59].

The main features of this method are the decoupling of the reaction equations using algebraic procedures and obtaining direct solution of the transformed equations. Thus, the kinetic models and their parameters can be identified in parallel for all reactions. The parameters are obtained via local optimization techniques.

In this chapter we introduce an alternative method where the heat balance equation is treated independently. Volume equation can be solved independently, but the ODE system (8.2) remains coupled. That is why we work in two stages: the concentrations system is rewritten as a decoupled extents system and the temperature equation is treated separately.

Then, the following system

$$\begin{cases} \dfrac{d\mathbf{y}}{dt} = \mathbf{f}(\theta, \mathbf{y}, \mathbf{z}, \boldsymbol{\Theta}) \text{ in } [0, T], \\ \mathbf{y}(0) = \mathbf{y}_0 \end{cases} \tag{8.2}$$

is replaced by its corresponding extents decoupled system

$$\begin{cases} \dfrac{d\mathbf{e}}{dt} = \mathbf{g}(\theta, \mathbf{e}, \mathbf{z}, \boldsymbol{\Theta}) \text{ in } [0, T], \\ \mathbf{e}(0) = \mathbf{0}, \end{cases} \tag{8.3}$$

where $\boldsymbol{\Theta}$ represents all the parameters to be identified and $\mathbf{g}$ is the source term that will be described in the next paragraphs.

The goal is to minimize the following functional cost in terms of extents

$$J_{m,l}(\boldsymbol{\Theta}_l^m) = \sum_{e \in \mathcal{E}} \sum_{s \in \mathcal{S}^e} |\hat{e}_{sl}^e - e_l^{(m)}(t_s^e, \boldsymbol{\Theta}_l^m)|^2, \forall m = 1, ..., M_l \text{ and } l = 1, ..., L, \tag{8.4}$$

where $\boldsymbol{\Theta}_{\boldsymbol{l}}^{\boldsymbol{m}}$ is the parameters vector, $e_l^{(m)}(t_s^e, \boldsymbol{\Theta}_l^m)$ and $\hat{e}_{sl}^e$ are the l-th component of the extents model and measurements, respectively at time $t_s^e \in S^e$ and experiment $e \in \mathcal{E}$. M_l is the set of kinetics for the l-th reaction.

To construct functions $J_{m,l}$ we need to define the extents as

$$\mathbf{e} = S\mathbf{y}$$

for a matrix $S \in \mathcal{M}_{L \times N}$, such that $SA = Id$ $S\mathrm{F}(0) = 0$ and $S\mathbf{y}_0 = \mathbf{0}$. The theory related to the matrix S is described in detail in [11].

Initially, we have a set of measurement species $\hat{\mathbf{y}}_s^e$, at time instants t_s^e, $s \in S^e$ and a set of experiments $e \in \mathcal{E}$. Then, we can compute $\hat{\mathbf{e}}_s^e = S\hat{\mathbf{y}}_s^e$ (observed extents) and also their derivatives $\dfrac{d\hat{\mathbf{e}}^e}{dt}$ using $\hat{\mathbf{e}}^e$ constructed as cubic splines of $e \in \mathcal{E}$.

Next, we need to construct model (8.3). Then, by multiplying mole balance system in (8.2) by S we have the ***extents*** model (8.3) and the source term defined by

$$\mathbf{g} = \boldsymbol{\delta}(\theta, \mathbf{y}, \mathbf{z}, \boldsymbol{\Theta}) + S\mathrm{F}\mathbf{f}^1 + \mathrm{f}^2\mathbf{e}.$$

Notice that this model is still coupled. So, we solve heat balance equation in parallel using

$$\hat{\boldsymbol{\delta}}^e = \frac{d\hat{\mathbf{e}}^e}{dt} - S\mathrm{F}\mathbf{f}^1 - \mathrm{f}^2\hat{\mathbf{e}}^e, \ e \in \mathcal{E}.$$

Then, we can solve heat balance equation independently to obtain $\hat{\theta}^e$, $e \in \mathcal{E}$.

Now, the solution of this problem is given by

$$\mathbf{e}(t,\Theta) = \int_0^t \exp\left(-\int_\tau^t \mathrm{f}^2(s)ds\right)\left[\boldsymbol{\delta}(\theta(\tau),\mathbf{y}(\tau),\mathbf{z}(\tau),\boldsymbol{\Theta}) + S\mathrm{F}(\tau)\mathbf{f^1}(\tau)\right]d\tau,$$

$\forall t \in [0,T]$ and it is solved using a numerical integration formula and replacing θ, $\mathbf{y}$, $\mathbf{z}$, F, $\mathbf{f^1}$ and f^2 by cubic splines of $\hat{\theta}^e$, $\mathbf{y}^e$, $\mathbf{z}^e$, F^e, $\mathbf{f}^{1e}$ and f^{2e} $e \in \mathcal{E}$.

Writing temperature in terms of extents in Batch reactors

Let us recall the extents ODE system in the case of a simple batch reactor with no heat exchange with the exterior as

$$\begin{cases} \dfrac{d\mathbf{e}}{dt} = \boldsymbol{\delta}, \\ \mathbf{e}(0) = \mathbf{e}_0. \end{cases} \tag{8.5}$$

Multiplying at the left by $\boldsymbol{\Delta}\mathbf{H}^t$ we get,

$$\frac{d\boldsymbol{\Delta}\mathbf{H}^t\mathbf{e}}{dt} = \boldsymbol{\Delta}\mathbf{H}^t\boldsymbol{\delta} = \rho c\frac{d\theta}{dt}. \tag{8.6}$$

Hence,

$$\frac{d(\boldsymbol{\Delta}\mathbf{H}^t\mathbf{e} - \rho c\theta)}{dt} = 0, \tag{8.7}$$

and so

$$\boldsymbol{\Delta}\mathbf{H}^t\mathbf{e} - \rho c\theta = constant = \boldsymbol{\Delta}\mathbf{H}^t\mathbf{0} - \rho c\theta_0 = -\rho c\theta_0. \tag{8.8}$$

This implies that

$$\theta(t) = \theta_0 + \frac{1}{\rho c}\boldsymbol{\Delta}\mathbf{H}^t\mathbf{e}(t). \tag{8.9}$$

Thus, we have an expression for θ in terms of the extent vector $\mathbf{e}$.
Moreover, since $\mathbf{e}(t) = S\mathbf{y}(t)$ we also have

$$\theta(t) = \theta_0 + \frac{1}{\rho c}\boldsymbol{\Delta}\mathbf{H}^t S\mathbf{y}(t) \tag{8.10}$$

an expression giving temperature in terms of the concentrations at each time instant.

8.4.2 Improvements in solution: The integral method.

Integral method allows to use experimental data in determining reaction rate parameters. But we do no use it in a local optimization only. An heuristic based on the variable neighbourhood search (VNS) [47] has been implemented. This method uses as initial values of the parameters those values previously computed using the incremental method. Thus, new solutions are generated doing successive perturbations both in kinetics and in parameters. The value of the integral functional cost is updated with the help of the derivatives computed via adjoint computation when a new combination of parameters and kinetic models improve the solution.

We describe the method in the following flow chart:

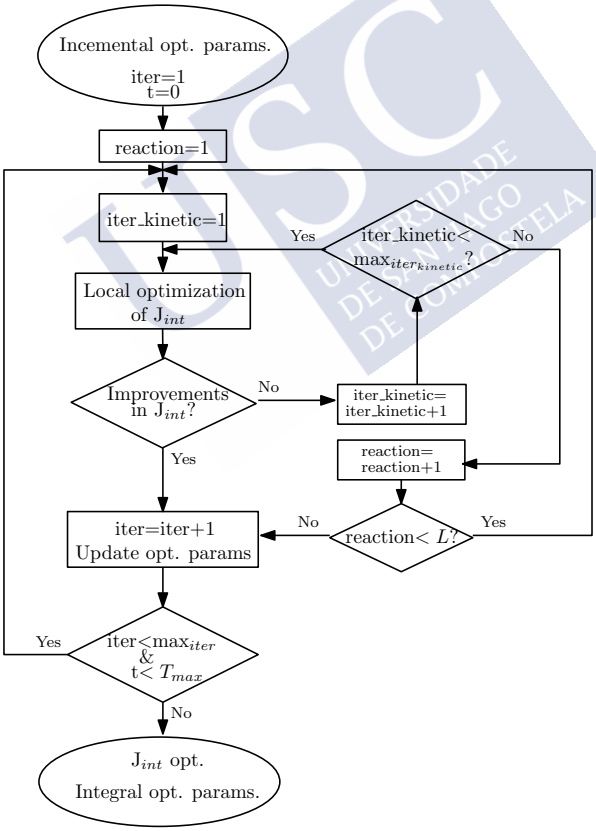

Figure 8.1: Flow chart VNS perturbations

The integral method

The integral method is based on a direct comparison of species measurements and computed concentrations via theoretical model. Sometimes, it also includes the comparison between experimental and theoretical temperatures. Due to this, integral method is obviously more time consuming.

The main difficulties lie in identifying the huge number of parameters which appear in the functional cost (we need to identify at the same time the parameters of each reaction) and in computing the derivatives of the functional cost with respect to these parameters.

Then candidate kinetic laws are integrated numerically and the parameters are calculated comparing experimental data and model prediction. We use a finite differences scheme described in Chapter 6 (BDF2 initialized with a BDF1) to solve the time derivative in the reactor model at each evaluation of the functional cost. Simultaneously, the derivatives of the functional cost are computed using the adjoint-state method we describe below.

Thus, the goal here is to minimize the following functional cost:

$$J_{int}(\boldsymbol{\Theta}) := \sum_{e\in\mathcal{E}}\sum_{i\in\mathcal{S}}\sum_{s\in S^e} \omega_{eis}(y_i^e(t_s^e,\boldsymbol{\Theta}) - \hat{y}_{si}^e)^2, \tag{8.11}$$

where $\boldsymbol{\Theta}$ is the parameters vector, $y_{si}^e(t_s^e,\boldsymbol{\Theta})$ and $\hat{y}_{si}^e$ are the i-th component of the solution of the model with parameters $\boldsymbol{\Theta}$ and of measurements, respectively at time $t_s^e \in S^e$ and experiment $e \in \mathcal{E}$.

The adjoint method

The adjoint method is a classical technique in optimal control theory. It has been successfully used for both chemical systems STR in [6] and PFR in [9].

For most local optimizers the derivatives of the cost function. To solve this, they are usually calculated using finite-difference formulas. The main problem is that the functional changes each time in the process and thus the computational time is greater. For this reason, the derivatives can be computed much more efficiently and accurately by the so-called ***adjoint method***. Of course, this method is related to the parameters appearing in chemical reaction models. There are two different approaches. When the adjoint method is applied to the continuous system (respectively, discretization scheme) it is called ***continuous adjoint approach*** (respectively, ***discrete adjoint approach***). In the implementation, we have used the second approach.

Throughout this section, we explain the use of the implemented computer program to compute the gradient of the *regularized* fitting function, i.e. that including the difference between theoretical and empirical concentrations.

Let us consider the following optimization problem:

$$\min_{\mathbf{u}} \hat{J}(\mathbf{u}) \tag{8.12}$$

s.a.

$$\begin{cases} \dfrac{d\mathbf{y}}{dt}(t) = \mathbf{f}(t, \mathbf{y}(t)) \ en \ [0,T], \\ \dfrac{d\mathbf{y}}{dt}(0) = \mathbf{y}_0, \end{cases}$$

being

$$\begin{aligned} \hat{J}(\mathbf{u}) = J(\mathbf{y}, \mathbf{u}) =& \|C\mathbf{y} - \hat{\mathbf{y}}\|_\omega^2 + z_B\|\mathbf{B}\|^2 + z_E\|\mathbf{E}\|^2 + z_G\|\mathbf{G}\|^2 \\ &+ z_\beta\|\boldsymbol{\beta}\|^2 + z_b\|\mathbf{b}\|^2 + z_\alpha\|\boldsymbol{\alpha}\|^2. \end{aligned} \tag{8.13}$$

In (8.13) C is the observation operator that extracts from the state $\mathbf{y}(t)$ their values at the observation times to be compared with the vector of observations, denoted by $\hat{\mathbf{y}}$. $\mathbf{B} = (B_1, ..., B_L)^t$ and $\mathbf{E} = (Ea_1, ..., Ea_L)^t$ denote the pre-exponential factor and the activation energy of the reactions. The rest of the parameters are:

$$\mathbf{G} = \left(G^1_{1,1}, ..., G^1_{1,P^1_1}, ..., G^1_{M_1,1}, ..., G^1_{M_1,P^1_{M_1}}, ..., G^L_{1,1}, ..., G^L_{M_L,P^L_{M_L}}\right)^t \in \mathbb{R}^{M_1P^1_{M_1}+...+M_LP^L_{M_L}},$$

$$\boldsymbol{\beta} = \left(\beta^1_{1,1,1}, ..., \beta^L_{M_L,P^L_{M_L},1}, \beta^1_{1,1,N}, ..., \beta^L_{M_L,P^L_{M_L},N}\right)^t \in \mathbb{R}^{N(M_1P^1_{M_1}+...+M_LP^L_{M_L})},$$

$$\mathbf{b} = \left(b^1_1, ..., b^1_{M_1}, ..., b^L_1, ..., b^L_{M_L}\right)^t \in \mathbb{R}^{M_1+...+M_L},$$

$$\boldsymbol{\alpha} = \left(\alpha^1_1, ..., \alpha^1_{M_1}, ..., \alpha^L_1, ..., \alpha^L_{M_L}\right)^t \in \mathbb{R}^{M_1+...+M_L}.$$

The source term in the ODE system represents one of the following expressions:

$$\begin{cases} A\boldsymbol{\delta}(\theta, \mathbf{y}) \text{ for a batch STR,} \\ A\boldsymbol{\delta}(\theta, \mathbf{y}) + \dfrac{1}{V}W\mathbf{u} - \dfrac{1}{V}\mathbf{y}\displaystyle\sum_{p=1}^{P} u^p \text{ for a CSTR.} \end{cases} \tag{8.14}$$

Notice that we have renamed the parameters vector called $\boldsymbol{\Theta}$ as $\mathbf{u}$ following the usual notation in control theory.

In addition, we have only considered species equations. That is because in most of the cases we are interested only in the adjustment of concentrations and also because the ranges of the species and the temperature are quite different. However, one can consider the entire system and also compute the gradient using the adjoint method. The only thing we should take into account is the

selection of good weights in the functional cost to avoid errors that can appear due to different ranges.

In the following paragraphs we calculate the gradient for the above problem, previously discretized, using the adjoint-system method.

1. **Building the state equation**

We need to construct a system for solving our problem. For this purpose, we use a finite-difference scheme called ***BDF2***. We obtain $N \times S - 1$ equations for $N \times S$ variables, so we need to introduce one more equation given by the BDF1 scheme. Both formulas are described in Chapter 6.

Now, we can write the state equation as follows:

$$B\mathbf{y} - \mathbf{b} = \mathbf{0} \text{ and } \mathbf{y} = (y_{11}, ..., y_{N1}, ..., y_{1S}, ..., y_{NS})^t, \tag{8.15}$$

with

$$B = \begin{pmatrix}
\frac{1}{h}I_{N\times N} & 0_{N\times N} & \cdots & \cdots & \cdots & \cdots & \cdots & 0_{N\times N} \\
-\frac{2}{h}I_{N\times N} & \frac{3}{2h}I_{N\times N} & 0_{N\times N} & \cdots & \cdots & \cdots & \cdots & 0_{N\times N} \\
\frac{1}{2h}I_{N\times N} & -\frac{2}{h}I_{N\times N} & \frac{3}{2h}I_{N\times N} & 0_{N\times N} & \cdots & \cdots & \cdots & 0_{N\times N} \\
0_{N\times N} & \ddots & \ddots & \ddots & \ddots & & & \vdots \\
\vdots & \ddots & \ddots & \ddots & \ddots & \ddots & & \vdots \\
\vdots & & \ddots & \ddots & \ddots & \ddots & \ddots & \vdots \\
\vdots & & & \ddots & \ddots & \ddots & \ddots & 0_{N\times N} \\
0_{N\times N} & \cdots & \cdots & \cdots & 0_{N\times N} & \frac{1}{2h}I_{N\times N} & -\frac{2}{h}I_{N\times N} & \frac{3}{2h}I_{N\times N}
\end{pmatrix},$$

$$\mathbf{b} = \begin{pmatrix}
\frac{1}{h}\begin{pmatrix} y_{0_1} \\ \vdots \\ y_{0_N} \end{pmatrix} + A\boldsymbol{\delta}(\theta(t_1), \mathbf{y}_1) \\
-\frac{1}{2h}\begin{pmatrix} y_{0_1} \\ \vdots \\ y_{0_N} \end{pmatrix} + A\boldsymbol{\delta}(\theta(t_2), \mathbf{y}_2) \\
A\boldsymbol{\delta}(\theta(t_3), \mathbf{y}_3) \\
\vdots \\
A\boldsymbol{\delta}(\theta(t_S), \mathbf{y}_S)
\end{pmatrix} \text{ in a batch STR,}$$

where $\mathbf{y}_s = (y_{1s}, ..., y_{Ns})^t$ $1 \leq s \leq S$, or

$$\mathbf{b} = \begin{pmatrix} \frac{1}{h}\begin{pmatrix} y_{0_1} \\ \vdots \\ y_{0_N} \end{pmatrix} + A\boldsymbol{\delta}(\theta(t_1), \mathbf{y}_1) \\ -\frac{1}{2h}\begin{pmatrix} y_{0_1} \\ \vdots \\ y_{0_N} \end{pmatrix} + A\boldsymbol{\delta}(\theta(t_2), \mathbf{y}_2) \\ A\boldsymbol{\delta}(\theta(t_3), \mathbf{y}_3) \\ \vdots \\ A\boldsymbol{\delta}(\theta(t_S), \mathbf{y}_S) \end{pmatrix} + \frac{1}{V}\begin{pmatrix} W\mathbf{u} - \mathbf{y}_1 \sum_{p=1}^{P} u^p(t_1) \\ W\mathbf{u} - \mathbf{y}_2 \sum_{p=1}^{P} u^p(t_2) \\ W\mathbf{u} - \mathbf{y}_3 \sum_{p=1}^{P} u^p(t_3) \\ \vdots \\ W\mathbf{u} - \mathbf{y}_S \sum_{p=1}^{P} u^p(t_S) \end{pmatrix}$$

in a CSTR.

2. **Building the adjoint-state equation**

We define $\mathbf{p} \in \mathbb{R}^{N \times S}$ as the solution of the following lineal system:

$$\mathbf{p}^t \partial_{\mathbf{y}} F(\mathbf{y}, \mathbf{u}) = \partial_{\mathbf{y}} J(\mathbf{y}, \mathbf{u}). \tag{8.16}$$

In the following, we calculate the above derivatives.

2.1. **Building the derivatives of state equation with respect to y**

In this case the derivatives also change if the reactor type changes. For a batch STR they can be written in matrix form as follows:

$$\partial_{\mathbf{y}} F(\mathbf{y}, \mathbf{u}) = B - \begin{pmatrix} AC_1 & & 0 \\ & \ddots & \\ 0 & & AC_S \end{pmatrix},$$

where each C_s for $1 \leq s \leq S$ is described by $(C_s)_{rn} = \dfrac{\partial \delta_r(\theta(t_s), \mathbf{y}_s)}{\partial y_n}$ $1 \leq r \leq L,\ 1 \leq n \leq N$ and partial derivatives can be easily computed as

$$\begin{aligned} \frac{\partial \delta_r(\theta(t_s), \mathbf{y}_s)}{\partial y_n} =& c_0(r) \sum_{j=1}^{M_r} \alpha_j^r \left(\sum_{m=1}^{P_j^r} G_{j,m}^r \beta_{j,m,n}^r y_{ns}^{\beta_{j,m,n}^r - 1} \prod_{\substack{k=1 \\ k \neq n}}^{N} y_{ks}^{\beta_{j,m,k}^r} \prod_{k=1}^{N_c} z_k(t_s)^{\beta_{j,m,k+N}^r} \right) \\ & \left(\sum_{m=1}^{P_j^r} G_{j,m}^r \prod_{k=1}^{N} y_{ks}^{\beta_{j,m,k}^r} \prod_{k=1}^{N_c} z_k(t_s)^{\beta_{j,m,k+N}^r} + b_j^r \right)^{\alpha_j^r - 1} c_1(r,j), \end{aligned} \tag{8.17}$$

with

$$c_0(r) = B_r exp\left(-\frac{E_{a_r}}{\mathcal{R}\theta(t_s)}\right),$$

$$c_1(r,j) = \prod_{\substack{k=1\\k\neq j}}^{M_r}\left(\sum_{m=1}^{P_k^r} G_{k,m}^r \prod_{n=1}^{N} y_{ns}^{\beta_{k,m,n}^r} \prod_{n=1}^{N_c} z_n^{\beta_{k,m,n+N}^r} + b_k^r\right)^{\alpha_k^r},$$

both evaluated in t_s.

For a CSTR the matrix of derivatives is the following:

$$\partial_{\mathbf{y}} F(\mathbf{y},\mathbf{u}) = B - \begin{pmatrix} AC_1 & & 0 \\ & \ddots & \\ 0 & & AC_S \end{pmatrix} - \frac{1}{V}\begin{pmatrix} \sum_{p=1}^{P} u^p(t_1) I & & 0 \\ & \ddots & \\ 0 & & \sum_{p=1}^{P} u^p(t_S) I \end{pmatrix}.$$

2.2. **Building derivatives of the fitting function with respect to y**

They can be written as a vector,

$$\partial_{\mathbf{y}} J(\mathbf{y},\mathbf{u}) = 2\left(y_{11} - \hat{y_{11}}, \cdots, y_{NS1} - \hat{y_{N1}}, \cdots, y_{1S} - \hat{y_{1S}}, \cdots, y_{NS} - \hat{y_{NS}}\right)^t.$$

3. **Building the gradient of the fitting function**

We define the gradient of the fitting function as,

$$\nabla_{\mathbf{y}} J(\mathbf{y},\mathbf{u}) = -\mathbf{p}^t \partial_{(\mathbf{u})} F(\mathbf{y},\mathbf{u}) + \partial_{(\mathbf{u})} J(\mathbf{y},\mathbf{u}). \tag{8.18}$$

In the following sections, we calculate the above derivatives.

3.1. **Building the derivatives of state equation with respect to u**

They can be written as a matrix,

$$\partial_{(\mathbf{u})} F(\mathbf{y},\mathbf{u}) = -\begin{pmatrix} AZ_1 \\ \vdots \\ AZ_S \end{pmatrix}$$

where each $Z_s,\ 1 \leq s \leq S$ has the following equation

$$Z_s = \begin{pmatrix} J_s^1 \middle| J_s^2 \middle| G^1_{1,1_s} \middle| \cdots \middle| G^L_{M_L,P^L_{M_L\,s}} \middle| \beta^1_{1,1,1_s} \middle| \cdots \middle| \beta^L_{M_L,P^L_{M_L},N_s} \middle| b^1_{1_s} \middle| \cdots \middle| b^L_{M_L\,s} \\ \middle| \alpha^1_{1_s} \middle| \cdots \middle| \alpha^L_{M_L\,s} \end{pmatrix}.$$

We describe below each of the derivatives in Z_s:

$$J_s^1 = \begin{pmatrix} exp\left(-\frac{E_{a_1}}{\mathcal{R}\theta(t_s)}\right) c_2(1) & & 0 \\ & \ddots & \\ 0 & & exp\left(-\frac{E_{a_L}}{\mathcal{R}\theta(t_s)}\right) c_2(L) \end{pmatrix}$$

with

$$c_2(r) = \prod_{j=1}^{M_r} \left(\sum_{m=1}^{P_j^r} G^r_{j,m} \prod_{n=1}^{N} y_{ns}^{\beta^r_{j,m,n}} \prod_{n=1}^{N_c} z_n(t_s)^{\beta^r_{j,m,n+N}} + b_j^r \right)^{\alpha_j^r} \text{ (evaluated in } t_s),$$

$$J_s^2 = \begin{pmatrix} -\frac{B_1}{\mathcal{R}\theta(t_s)} exp\left(-\frac{E_{a_1}}{\mathcal{R}\theta(t_s)}\right) c_2(1) & & 0 \\ & \ddots & \\ 0 & & -\frac{B_L}{\mathcal{R}\theta(t_s)} exp\left(-\frac{E_{a_L}}{\mathcal{R}\theta(t_s)}\right) c_2(L) \end{pmatrix},$$

$$G^r_{j,m_s} = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ c_0(r)\alpha_j^r \left(\sum_{m=1}^{P_j^r} G^r_{j,m} \prod_{n=1}^{N} y_{ns}^{\beta^r_{j,m,n}} \prod_{n=1}^{N_c} z_n(t_s)^{\beta^r_{j,m,n+N}} + b_j^r \right)^{\alpha_j^r - 1} \\ \prod_{n=1}^{N} y_{ns}^{\beta^r_{j,m,n}} \prod_{n=1}^{N_c} z_n(t_s)^{\beta^r_{j,m,n+N}} c_1(r,j) \\ 0 \\ \vdots \\ 0 \end{pmatrix},$$

$$\beta^r_{j,m,n_s} = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ c_0(r)\sum_{j=1}^{M_r}\alpha_j^r\left(\sum_{m=1}^{P_j^r} G^r_{j,m}\prod_{k=1}^{N} y_{ks}^{\beta^r_{j,m,k}}\prod_{k=1}^{N_c} z_k(t_s)^{\beta^r_{j,m,k+N}} + b_j^r\right)^{\alpha_j^r-1} \\ \left(\sum_{m=1}^{P_j^r} G^r_{j,m}\log(\beta^r_{j,m,n}) y_{ns}^{\beta^r_{j,m,n}}\prod_{\substack{k=1\\k\neq n}}^{N} y_{ks}^{\beta^r_{j,m,k}}\prod_{k=1}^{N_c} z_k(t_s)^{\beta^r_{j,m,k+N}}\right) c_1(r,j) \\ 0 \\ \vdots \\ 0 \end{pmatrix},$$

$$b^r_{j_s} = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ c_0(r)\alpha_j^r\left(\sum_{m=1}^{P_j^r} G^r_{j,m}\prod_{n=1}^{N} y_{ns}^{\beta^r_{j,m,n}}\prod_{n=1}^{N_c} z_n(t_s)^{\beta^r_{j,m,n+N}} + b_j^r\right)^{\alpha_j^r-1} c_1(r,j) \\ 0 \\ \vdots \\ 0 \end{pmatrix},$$

and

$$\alpha^r_{j_s} = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ c_0(r)\log\left(\sum_{m=1}^{P_j^r} G^r_{j,m}\prod_{n=1}^{N} y_{ns}^{\beta^r_{j,m,n}}\prod_{n=1}^{N_c} z_n(t_s)^{\beta^r_{j,m,n+N}} + b_j^r\right) c_2(r) \\ 0 \\ \vdots \\ 0 \end{pmatrix}.$$

3.2. **Building derivatives of the fitting function with respect to u**

They can be written as a vector,

$$\partial_{\mathbf{y}} J(\mathbf{y},\mathbf{u}) = 2\left(Z_b B_1, \cdots, Z_B B_L, \cdots, Z_\alpha \alpha_l^1, \cdots, Z_\alpha \alpha_{M_L}^L\right)^t.$$

4. **Adjoint method flow chart**

Figure 8.2 shows the flow chart of the program which calculates the value of the fitting function, and its partial derivatives with respect to the involved parameters.

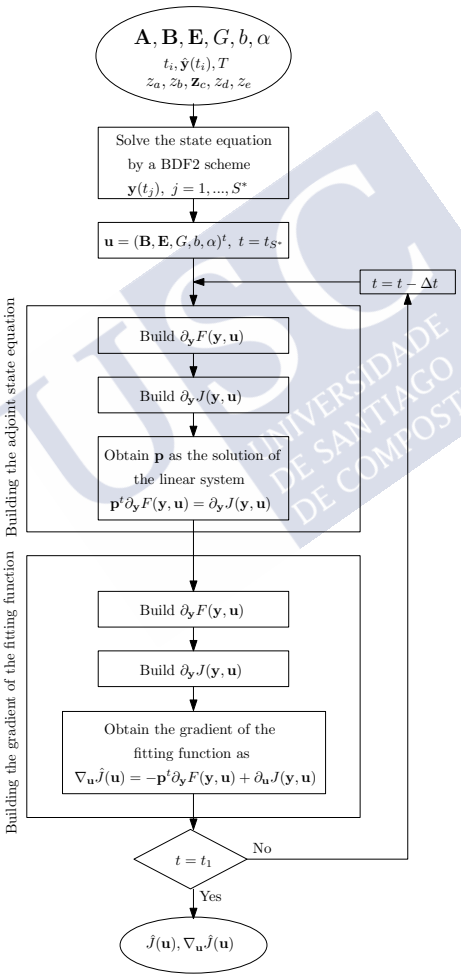

Figure 8.2: Flow chart for a batch STR adjoint method

8.5 An example

We consider an academic example that represents a batch type reactor with known temperature. The reaction system is described by 12 species, involved in 6 reactions and 1 catalyst with constant concentration equals to 0.001 mol/l.

$$\begin{aligned} A + B &\rightarrow C + D, \\ B &\rightarrow C + 0.5E, \\ B &\rightarrow F + G, \\ B &\rightarrow H + I, \\ B &\rightarrow J + K, \\ D + G &\rightarrow L. \end{aligned} \tag{8.19}$$

The data related to these species and its reactions is represented in the following image:

Global data, REQUIRED														
Reactor	Type	BatchSTR												
	Transient state	y												
	Computed temperature	n												
Species	Number	12												
	Observed	12												
	Name (12)	A	B	C	D	E	F	G	H	I	J	K	L	
	Observed species (y/n)	y	y	y	y	y	y	y	y	y	y	y	y	
Catalysts	Number	1												
	Name (1)	Cat												
Reactions	Number	6												
Experiments	Number	10												
Thermal data (only when temperature is computed), NOT REQUIRED														
Species	Molecular weigths, kg/kmol (12)	0.05	0.14	0.12	0.07	0.04	0.122	0.018	0.07	0.07	0.09	0.05	0.088	
	Specific heat, J/kg K (12)	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	
Reactions	Temperature, K	298.15												
	Reaction heat at 298.15 K, J/kmol (6)	1.5	1	0.8	0.7	0.6	0.5							
Heat transfer	Overall coefficient, W/K	6												
Temperature	Measurements	y												

Figure 8.3: Species and reactions data

We have 10 experiments with different initial conditions and time measurements from 0 to 100 seconds at each 10 seconds. An example of the measurements in one of these experiments is represented in the following picture:

Times, s	Catalysts	State/Outlet												
	Concentration, mol/l	Concentration, mol/l												Temperature, K
	Cat	A	B	C	D	E	F	G	H	I	J	K	L	
Fill	Fill	Fill	Fill	Fill	Fill	Fill	Fill	Fill	Fill	Fill	Fill	Fill	Fill	Fill
0	0.001	1	2	0	0	0	0	0	0	0	0	0	0	373
10	0.001	0.4791859	0.6746524	1.2787301	0.5207603	0.378958	0.0465967	0.0465428	2.088E-05	2.088E-05	1.713E-10	1.713E-10	5.385E-05	365.0226243
20	0.001	0.3770251	0.4598384	1.4868189	0.6228381	0.431922	0.0533161	0.0531793	2.663E-05	2.663E-05	2.047E-10	2.047E-10	0.0001367	357.915025
30	0.001	0.3341356	0.3769871	1.5672218	0.6656607	0.4506787	0.055762	0.0555583	2.913E-05	2.913E-05	2.153E-10	2.153E-10	0.0002037	351.584541
40	0.001	0.311079	0.3347217	1.6082825	0.6886674	0.4596807	0.0569653	0.0567117	3.042E-05	3.042E-05	2.195E-10	2.195E-10	0.0002536	345.9460747
50	0.001	0.2970009	0.3098537	1.6324593	0.7027085	0.4647301	0.0576558	0.0573652	3.116E-05	3.116E-05	2.213E-10	2.213E-10	0.0002906	340.9239456
60	0.001	0.2876827	0.2938516	1.6480249	0.711999	0.4678538	0.0580919	0.0577736	3.161E-05	3.161E-05	2.222E-10	2.222E-10	0.0003183	336.4507705
70	0.001	0.281149	0.282881	1.6587005	0.7185116	0.4699247	0.0583866	0.0580472	3.191E-05	3.191E-05	2.227E-10	2.227E-10	0.0003394	332.4665399
80	0.001	0.2763592	0.2749861	1.6663856	0.7232849	0.4713724	0.0585961	0.0582403	3.211E-05	3.211E-05	2.229E-10	2.229E-10	0.0003559	328.9178068
90	0.001	0.2727185	0.2690779	1.6721384	0.7269126	0.4724285	0.0587514	0.0583825	3.225E-05	3.225E-05	2.231E-10	2.231E-10	0.0003689	325.7569675
100	0.001	0.2698656	0.2645092	1.676588	0.7297549	0.4732268	0.0588705	0.058491	3.236E-05	3.236E-05	2.232E-10	2.232E-10	0.0003795	322.9416227

Figure 8.4: Experimental data set

The list of kinetics for each reaction is:

Reaction 1

$$\delta_1^{(1)}(\theta,\mathbf{y},\mathbf{z}) = B_1 e^{\left(-\frac{Ea_1}{R\theta}\right)} y_1^{\alpha_1} y_2^{\alpha_2} z_1^{\alpha_3},$$
$$\delta_1^{(2)}(\theta,\mathbf{y},\mathbf{z}) = B_1 e^{\left(-\frac{Ea_1}{R\theta}\right)} y_1^{\alpha_1} z_1^{\alpha_2},$$
$$\delta_1^{(3)}(\theta,\mathbf{y},\mathbf{z}) = B_1 e^{\left(-\frac{Ea_1}{R\theta}\right)} y_2^{\alpha_1} z_1^{\alpha_2},$$
$$\delta_1^{(4)}(\theta,\mathbf{y},\mathbf{z}) = B_1 e^{\left(-\frac{Ea_1}{R\theta}\right)} y_1^{\alpha_1} y_2^{\alpha_2},$$
$$\delta_1^{(5)}(\theta,\mathbf{y},\mathbf{z}) = B_1 e^{\left(-\frac{Ea_1}{R\theta}\right)} y_1^{\alpha_1},$$
$$\delta_1^{(6)}(\theta,\mathbf{y},\mathbf{z}) = B_1 e^{\left(-\frac{Ea_1}{R\theta}\right)} y_2^{\alpha_1},$$
$$\delta_1^{(7)}(\theta,\mathbf{y},\mathbf{z}) = B_1 e^{\left(-\frac{Ea_1}{R\theta}\right)} z_1^{\alpha_1},$$
$$\delta_1^{(8)}(\theta,\mathbf{y},\mathbf{z}) = B_1 e^{\left(-\frac{Ea_1}{R\theta}\right)} y_1^{\alpha_1^{int}} y_2^{\alpha_2^{int}} z_1^{\alpha_3^{int}}.$$

Reaction 2

$$\delta_2^{(1)}(\theta,\mathbf{y},\mathbf{z}) = B_2 e^{\left(-\frac{Ea_2}{R\theta}\right)} y_2^{\alpha_1} z_1^{\alpha_2},$$
$$\delta_2^{(2)}(\theta,\mathbf{y},\mathbf{z}) = B_2 e^{\left(-\frac{Ea_2}{R\theta}\right)} y_2^{\alpha_1},$$
$$\delta_2^{(3)}(\theta,\mathbf{y},\mathbf{z}) = B_2 e^{\left(-\frac{Ea_2}{R\theta}\right)} z_1^{\alpha_1},$$
$$\delta_2^{(4)}(\theta,\mathbf{y},\mathbf{z}) = B_2 e^{\left(-\frac{Ea_2}{R\theta}\right)} y_2^{\alpha_1^{int}} z_1^{\alpha_2}.$$

Reaction 3

$$\delta_3^{(1)}(\theta,\mathbf{y},\mathbf{z}) = B_3 e^{\left(-\frac{Ea_3}{R\theta}\right)} y_2^{\alpha_1} z_1^{\alpha_2},$$
$$\delta_3^{(2)}(\theta,\mathbf{y},\mathbf{z}) = B_3 e^{\left(-\frac{Ea_3}{R\theta}\right)} y_2^{\alpha_1},$$
$$\delta_3^{(3)}(\theta,\mathbf{y},\mathbf{z}) = B_3 e^{\left(-\frac{Ea_3}{R\theta}\right)} z_1^{\alpha_1},$$
$$\delta_3^{(4)}(\theta,\mathbf{y},\mathbf{z}) = B_3 e^{\left(-\frac{Ea_3}{R\theta}\right)} y_2^{\alpha_1^{int}} z_1^{\alpha_2},$$
$$\delta_3^{(5)}(\theta,\mathbf{y},\mathbf{z}) = B_3 e^{\left(-\frac{Ea_3}{R\theta}\right)} y_2^{\alpha_1} z_1^{\alpha_2^{int}},$$
$$\delta_3^{(6)}(\theta,\mathbf{y},\mathbf{z}) = B_3 e^{\left(-\frac{Ea_3}{R\theta}\right)} y_2^{\alpha_1^{int}} z_1^{\alpha_2^{int}}.$$

Reaction 4

$$\delta_4^{(1)}(\theta,\mathbf{y},\mathbf{z}) = B_4 e^{\left(-\frac{Ea_4}{R\theta}\right)} y_2^{\alpha_1} z_1^{\alpha_2},$$
$$\delta_4^{(2)}(\theta,\mathbf{y},\mathbf{z}) = B_4 e^{\left(-\frac{Ea_4}{R\theta}\right)} y_2^{\alpha_1},$$
$$\delta_4^{(3)}(\theta,\mathbf{y},\mathbf{z}) = B_4 e^{\left(-\frac{Ea_4}{R\theta}\right)} z_1^{\alpha_1},$$
$$\delta_4^{(4)}(\theta,\mathbf{y},\mathbf{z}) = B_4 e^{\left(-\frac{Ea_4}{R\theta}\right)} y_2^{\alpha_1^{int}} z_1^{\alpha_2}.$$

Reaction 5

$$\delta_5^{(1)}(\theta,\mathbf{y},\mathbf{z}) = B_5 e^{\left(-\frac{Ea_5}{R\theta}\right)} y_2^{\alpha_1} z_1^{\alpha_2},$$
$$\delta_5^{(2)}(\theta,\mathbf{y},\mathbf{z}) = B_5 e^{\left(-\frac{Ea_5}{R\theta}\right)} y_2^{\alpha_1},$$
$$\delta_5^{(3)}(\theta,\mathbf{y},\mathbf{z}) = B_5 e^{\left(-\frac{Ea_5}{R\theta}\right)} z_1^{\alpha_1},$$
$$\delta_5^{(4)}(\theta,\mathbf{y},\mathbf{z}) = B_5 e^{\left(-\frac{Ea_5}{R\theta}\right)} y_2^{\alpha_1^{int}} z_1^{\alpha_2}.$$

Reaction 6

$$\delta_6^{(1)}(\theta,\mathbf{y},\mathbf{z}) = B_6 e^{\left(-\frac{Ea_6}{R\theta}\right)} y_4^{\alpha_1} y_7^{\alpha_2} z_1^{\alpha_3},$$
$$\delta_6^{(2)}(\theta,\mathbf{y},\mathbf{z}) = B_6 e^{\left(-\frac{Ea_6}{R\theta}\right)} y_4^{\alpha_1} y_7^{\alpha_2},$$
$$\delta_6^{(3)}(\theta,\mathbf{y},\mathbf{z}) = B_6 e^{\left(-\frac{Ea_6}{R\theta}\right)} y_7^{\alpha_1} z_1^{\alpha_2},$$
$$\delta_6^{(4)}(\theta,\mathbf{y},\mathbf{z}) = B_6 e^{\left(-\frac{Ea_6}{R\theta}\right)} y_4^{\alpha_1} z_1^{\alpha_2},$$
$$\delta_6^{(5)}(\theta,\mathbf{y},\mathbf{z}) = B_6 e^{\left(-\frac{Ea_6}{R\theta}\right)} y_4^{\alpha_1},$$
$$\delta_6^{(6)}(\theta,\mathbf{y},\mathbf{z}) = B_6 e^{\left(-\frac{Ea_6}{R\theta}\right)} y_7^{\alpha_1},$$
$$\delta_6^{(7)}(\theta,\mathbf{y},\mathbf{z}) = B_6 e^{\left(-\frac{Ea_6}{R\theta}\right)} z_1^{\alpha_1},$$
$$\delta_6^{(8)}(\theta,\mathbf{y},\mathbf{z}) = B_6 e^{\left(-\frac{Ea_6}{R\theta}\right)} y_4^{\alpha_1^{int}} y_7^{\alpha_2^{int}} z_1^{\alpha_3}.$$

R is the universal gas constant, $B \in [0, 10^{14}]$ and $Ea \in [0, 200000]$ represent the pre-exponential factor and the activation energy, respectively in the Arrhenius law, and $\alpha_i \in [0, 2]$ $\forall i = 1, 2, 3$. The super index int in the exponents means that we do integer optimization on these parameters.

The incremental method selects the following kinetics after computing the parameters of all the kinetics in the list in about 4732 seconds

$$\delta_1^{(4)}(\theta,\mathbf{y},\mathbf{z}) = 1.76\ 10^5 e^{\left(-\frac{4.60\ 10^5}{R\theta}\right)} y_1^{0.92} y_2^{0.90},\ \text{with}\ J_{4,1}(\boldsymbol{\Theta}_1^4) = 5.48\ 10^{-2},$$
$$\delta_2^{(2)}(\theta,\mathbf{y},\mathbf{z}) = 1.06\ 10^4 e^{\left(-\frac{3.80\ 10^4}{R\theta}\right)} y_2^{1.87},\ \text{with}\ J_{2,2}(\boldsymbol{\Theta}_2^2) = 5.48\ 10^{-2},$$
$$\delta_3^{(2)}(\theta,\mathbf{y},\mathbf{z}) = 201.29 e^{\left(-\frac{3.80\ 10^4}{R\theta}\right)} y_2^{1.88},\ \text{with}\ J_{2,3}(\boldsymbol{\Theta}_3^2) = 5.48\ 10^{-2},$$
$$\delta_4^{(2)}(\theta,\mathbf{y},\mathbf{z}) = 1.16\ 10^4 e^{\left(-\frac{1.14\ 10^5}{R\theta}\right)} y_2^{0.93},\ \text{with}\ J_{2,4}(\boldsymbol{\Theta}_4^2) = 5.48\ 10^{-2},$$
$$\delta_5^{(1)}(\theta,\mathbf{y},\mathbf{z}) = 1.62\ 10^8 e^{\left(-\frac{1.14\ 10^5}{R\theta}\right)} y_2^{0.95} z_1^{0.96},\ \text{with}\ J_{1,5}(\boldsymbol{\Theta}_5^1) = 5.48\ 10^{-2},$$
$$\delta_6^{(2)}(\theta,\mathbf{y},\mathbf{z}) = 2.27\ 10^6 e^{\left(-\frac{6.86\ 10^4}{R\theta}\right)} y_4^{0.98} y_7^{0.97},\ \text{with}\ J_{2,6}(\boldsymbol{\Theta}_6^2) = 5.48\ 10^{-2}.$$

The objective value of the integral method for these kinetics is 0.2184.

The integral method provides a value of the functional cost of 0.2071 after 11755 seconds. The selected kinetics are the following:

$$\delta_1^{(8)} = 1.97\ 10^8 e^{\left(-\frac{4.60\ 10^4}{R\theta}\right)} y_1 y_2 z_1,$$
$$\delta_2^{(1)} = 1.05\ 10^7 e^{\left(-\frac{3.80\ 10^4}{R\theta}\right)} y_2^{1.87} z_1^{0.99},$$
$$\delta_3^{(4)} = 6.46\ 10^4 e^{\left(-\frac{3.44\ 10^4}{R\theta}\right)} y_2^2 z_1^{0.84},$$
$$\delta_4^{(2)} = 1.16\ 10^4 e^{\left(-\frac{6.9710^4}{R\theta}\right)} y_2^{0.93},$$
$$\delta_5^{(4)} = 7.99\ 10^8 e^{\left(-\frac{1.18\ 10^5}{R\theta}\right)} y_2 z_1^{1.02},$$
$$\delta_6^{(8)} = 4.96\ 10^9 e^{\left(-\frac{6.91\ 10^4}{R\theta}\right)} y_4 z_1^{1.09}.$$

In Figures 8.5 and 8.6 we can see the comparison between the data and the numerical solution of the model with the selected kinetics and their parameters in both incremental and integral methods in one of the experiments.

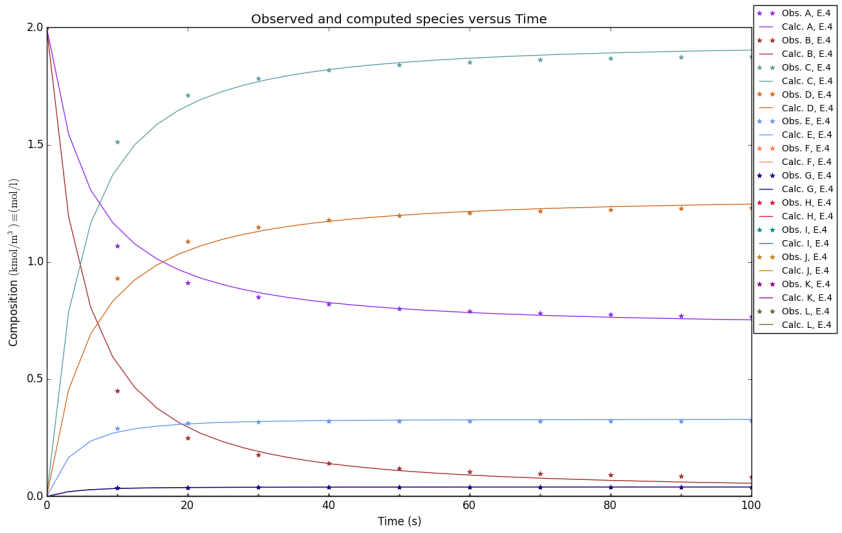

Figure 8.5: Numerical vs Experimental concentrations: Incremental method

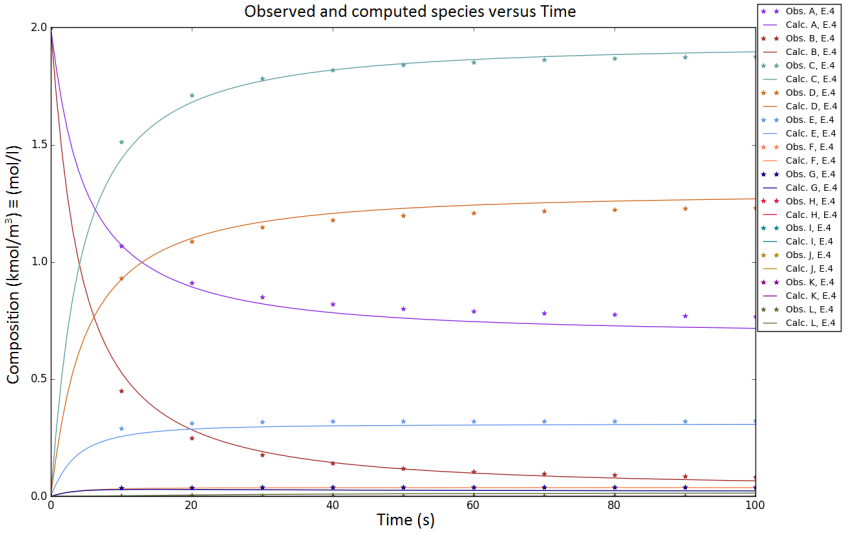

Figure 8.6: Numerical vs Experimental concentrations: Integral method

The incremental method provides a good solution as it can be seen in Figure 8.5. However, experimental measurements are not compared directly in this method because an algebraic transformation of the data was previously done. Then, the integral method is used to correct these possible differences between data and numerical solution. The largest differences appear in species A, E and F. It is not recommendable to use only the integral method by itself because it is computationally expensive.

In fact, these methods generate better results when used together. The incremental method provides good results when enough measurements and/or experiments (not affected by noise) are given. In other cases, incremental method generates an initial solution for the integral method which is essential in order to obtain a better adjustment. Moreover, this last method is computationally expensive and so, to improve this, an adjoint method is considered for computing functional cost derivatives and a VNS heuristic is also considered in the optimization process to select faster the best combination of kinetic models from the catalogue.

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Conclusions

In conclusion, a tandem of two methods has been used. The first technique, called incremental method, is a methodology able to decouple the model for working separately with each kinetic. Then, the identification problem is divided into a set of smaller subproblems, one for each kinetic. The second technique, called integral method, is an heuristic based on the variable neighbourhood search (VNS). This method uses as initial values of the parameters those previously computed by the incremental method. New solutions are generated by optimizing the integral functional cost and updating the parameters by doing successive perturbations both in kinetics and in parameters. The derivatives of this functional cost are computed via the adjoint method, as integral method by itself is time consuming. When the value of the functional cost decreases means that a new combination of parameters and kinetic models improve the solution. The use of both incremental and integral methods, with the help of adjoints calculation, provides good results in the identification of kinetic models, as exemplified for batch reactor.

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Future work

To conclude the dissertation of this thesis, we briefly introduce some of the research lines that we would like to develop as part of future research:

- Existence of solution of the full convection-diffusion-reaction model

  Prove the existence of solution of the full model, including the equation of temperature. The property of boundedness of total mass needs an analogous one for the energy equation. Then, we need to explore a different approach for the complete system.

- Existence of solution of the FBR model

  It is a more complex model, with the added difficulty of coupling between the macro-scale and the micro-scale model. Therefore, we should study the most appropriate techniques for treating this problem.

- Identification of parameters in the reaction term

  The problem of identification of parameters for this type of reactors can be addressed. The ideal approach is to do it in two phases. In the first one, the identification of the stationary model can be studied to later treat the transient one. In this reactor the most adequate method is the integral. But it is important to take into account the computation time. Maybe the adjoint method must be used too. The residence time in this type of reactor is large in most of the cases. Then probably only in the first time steps the transient model is needed.

- Deactivation of the catalyst

  In many cases it is assumed that the effectiveness of the catalysts for increasing the speed of the reactions does not change over time. Sometimes that is not truth, because the activity decreases as the catalyst is used. Sometimes this procedure is very fast, in other cases it is so slow that regeneration or replacement of the catalyst is only necessary after a long period of time. That is an interesting phenomena to include in the model and then study it.

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Appendix A

Summary of equations of continuum thermomechanics

We recall the general equations of continuum thermomechanics for reacting mixtures. Further details can be found, for instance, in [8].

A.1 Equations of continuum thermomechanics

Species mass

$$\frac{\partial(\rho Y_i)}{\partial t} + \mathrm{div}(\rho Y_i \mathbf{v}) - \mathrm{div}(\rho \mathcal{D}_i \mathrm{grad} Y_i) = \mathcal{M}_i \sum_{j=1}^{R} a_{ij} \delta_j(\theta, \mathbf{y}),\ i = 1, ..., N. \quad \text{(A.1)}$$

Mixture mass

$$\frac{\partial \rho}{\partial t} + \mathrm{div}(\rho \mathbf{v}) = 0. \quad \text{(A.2)}$$

Momentum

$$\frac{\partial(\rho \mathbf{v})}{\partial t} + \mathrm{div}(\rho \mathbf{v} \otimes \mathbf{v}) = \mathrm{div} T + \mathbf{b}. \quad \text{(A.3)}$$

Energy

$$\frac{\partial(\rho e)}{\partial t} + \mathrm{div}(\rho e \mathbf{v}) + \mathrm{div}\mathbf{q} = T \cdot D + f. \quad \text{(A.4)}$$

Constitutive equations (ideal solution)

We assume that the mixture density can change due to change in composition and/or temperature. More precisely, we make the following assumptions:

- The mixture is an ideal solution and then its volume is the sum of the volumes occupied by the species if they were isolated.
- The density of each pure species only depends on temperature. For the i-th species it will be called d_i.

Then it is easy to see that the density is given by

$$\rho = \left(\sum_{i=1}^{N} \frac{Y_i}{d_i} \right)^{-1} \quad (kg/m^3), \tag{A.5}$$

with $d_i = \hat{d}_i(\theta)$. Indeed, the specific volume $\nu = 1/\rho$ is the volume occupied by 1 kg of mixture. Since the mass of the i-th species in this kg is Y_i kg, then its volume is Y_i/d_i m^3. Therefore, the total volume of 1 kg of mixture is

$$\nu = \sum_{i=1}^{N} \frac{Y_i}{d_i}.$$

Since $y_i = \rho Y_i / \mathcal{M}_i$, then equation (A.5) is equivalent to

$$1 = \sum_{i=1}^{N} \frac{\mathcal{M}_i y_i}{d_i}. \tag{A.6}$$

Constitutive equations (for mixture of perfect gases)

If we deal with a mixture of perfect gases, then

$$p = \rho R \theta, \tag{A.7}$$

where R is the gas constant given by

$$R = \frac{\mathcal{R}}{\mathcal{M}}$$

and $\mathcal{M}$ is the molecular mass of the mixture defined by

$$\frac{1}{\mathcal{M}} = \sum_{i=1}^{N} \frac{Y_i}{\mathcal{M}_i}.$$

Moreover, in both cases (ideal solution or mixture of perfect gases) we have

$$
\begin{aligned}
&e = \sum_{i=1}^{N} Y_i e_i, \text{ with } e_i = \hat{e}_i(\theta), \quad (J/kg) \\
&\mathbf{q} = -k \operatorname{grad} \theta \text{ (Fourier's law)}, \quad (W/m^2), \\
&c_i = \hat{c}_i(\theta) = \frac{\partial \hat{e}_i}{\partial \theta}(\theta) \text{ (specific heat)}, \ (J/(kgK)), \\
&T = -pI + T_v, \text{ with } T_v = 2\eta D \text{ (the viscous stress tensor) } (N/m^2).
\end{aligned}
\tag{A.8}
$$

Notations

ρ: density (kg/m^3)

$\mathbf{v}$: velocity (m/s)

p: presure (N/m^2)

η, ξ: viscosity coefficients (Ns/m^2)

$\mathbf{b}$: density of body force (N/m^3)

$D = \frac{1}{2}(\text{grad}\mathbf{v} + \text{grad}\mathbf{v}^t)$ (strain rate) (s^{-1})

Y_i: mass fraction of the i-th species

y_i: concentration of the i-th species, $y_i = \rho Y_i / \mathcal{M}_i$ $(kmol/m^3 = mol/l)$

d_i: density of the i-th pure species (kg/m^3)

$\mathcal{D}_i$: diffusion coefficient of the i-th species (m^2/s)

δ_j: kinetic of the j-th reaction $(kmol/(m^3 s))$

$\mathcal{M}_i$: molecular mass of the i-th species $(kg/kmol)$

R: gas constant $(J/(kgK))$

$\mathcal{R}$: universal gas constant (8314.4621 $J/(kmolK)$)

$\mathcal{M}$: molecular mass of the mixture

e: specific internal energy (J/kg)

$\mathbf{q}$: density of the heat flux vector (W/m^2)

θ: absolute temperature (K)

$A = (a_{ij})$: stoichiometric matrix

Remark A.1.1. *By replacing the constitutive equation (A.5) in the mass conservation equation (A.2), we get a condition for the divergence of the velocity in terms of the mixture temperature and composition. Coupled with the momentum equation (A.3) it can be used to determine pressure.*

Remark A.1.2. *Thus, in order to solve the models we could use a segregated method. Firstly, for a given temperature (θ) and composition Y_i we can compute density by (A.5) and then solve the momentum equation to determine velocity and pressure. Next, by using the computed velocity we can solve the species conservation equations (A.1) and the energy equation (A.4) to determine mass fractions and temperature, respectively.*

Appendix B

Abstract semilinear initial-value problems

This appendix has been extracted from [42] (see also [43]).

B.1 Operators. Spectrum and resolvent

Throughout this section $X \neq \{0\}$ is a real or complex Banach space and $L(X)$ denote the Banach space of the bounded linear operators form X into itself. Even in the case where X is a real vector space, we need to deal with complex spectrum and resolvent: so we introduce the complexification of X, defined as

$$\tilde{X} = \{x + iy : x,\ y \in X\};\ \|x + iy\|_{\tilde{X}} = \sup_{0 \leq \theta \leq 2\pi} \|x \cos\theta + y \sin\theta\|.$$

If A: $D(A) \subset X \mapsto X$ is a linear operator, the complexification of A is defined by

$$D(\tilde{A}) = \{x + iy : x,\ y \in D(A)\},\quad \tilde{A}(x + iy) = Ax + iAy.$$

In the sequel if no confusion will arise we shall drop out all the tildes, and by spectrum and resolvent of A we shall mean spectrum and resolvent of $\tilde{A}$.

Definition B.1.1. *Let $A : D(A) \subset X \mapsto X$ be a linear operator. The resolvent set $\rho(A)$ and the spectrum $\sigma(A)$ of A are defined by*

$$\rho(A) = \{\lambda \in \mathbb{C}\ :\ \exists (\lambda I - A)^{-1} \in L(X)\}, \sigma(A) = \mathbb{C} \backslash \rho(A).$$

If $\lambda \in \rho(A)$, we set

$$R(\lambda, A) := (\lambda I - A)^{-1}$$

and $R(\lambda, A)$ is called resolvent operator or simply resolvent.

B.2 Sectorial operators

Definition B.2.1. *We say that a linear operator A: $D(A) \subset X \to X$ is sectorial if there are constants $\omega \in \mathbb{R}$, $\theta \in (\pi/2,\ \pi)$, $M > 0$ such that*

$$\rho(A)\ \supset S_{\theta,\omega}\ := \{\lambda \in \mathbb{C} : \lambda \neq \omega,\ |\arg(\lambda - \omega)|\ < \theta\}, \tag{B.1}$$

$$\|R(\lambda,\ A)\|_{L(X)}\ \leq\ \frac{M}{|\lambda - \omega|},\ \lambda \in S_{\theta,\omega}, \tag{B.2}$$

where the set $S_{\theta,\omega}$ is represented in the following graph:

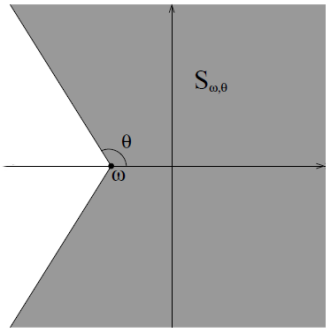

Figure B.1: Sector image

Proposition B.2.1. *Let $A : D(A) \subset X \to X$ be a linear operator such that $\rho(A)$ contains a halfplane $\{\lambda \in \mathbb{C}\ :\ \mathrm{Re}\lambda \geq \omega\}$, and*

$$\|\lambda R(\lambda, A)\|_{L(X)}\ \leq M,\ \mathrm{Re}\lambda \geq \omega,$$

with $\omega \geq 0, M \geq 1$. Then A is sectorial.

For every $t > 0$, Definition B.2.1 above allows us to define, for any sectorial operator A, a bounded linear operator e^{tA} on X, through an integral formula. For $r > 0, \eta \in (\pi/2,\ \theta)$, in the curve $\gamma_{r,\eta}$ defined by

$$\{\lambda \in \mathbb{C}\ :\ |\arg\lambda| = \eta,\ |\lambda|\ \geq r\} \cup \{\lambda \in \mathbb{C}\ :\ |\arg\lambda|\ \leq \eta,\ |\lambda|\ = r\},$$

oriented counterclockwise, as in Figure B.2.

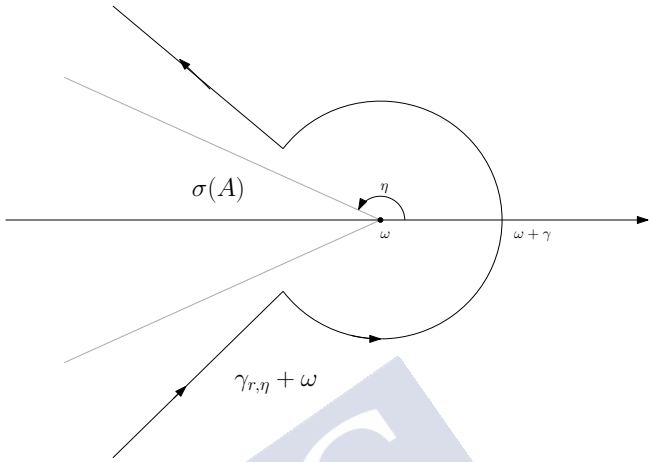

Figure B.2: Curve $\gamma_{r,\eta}+\omega$

Definition B.2.2. *Let A be a sectorial operator. The function*

$$t \in [0,\infty) \to e^{tA} \in L(X)$$

defined by means of the Dunford integral

$$e^{tA} = \frac{1}{2\pi i}\int_{\gamma_{r,\eta}+\omega} e^{t\lambda}R(\lambda,\ A)d\lambda,\ t>0$$

is called the analytic semigroup generated by A in X and $e^{0A}=I$.

B.3 Second order differential operators

Let us consider general second order elliptic operators in an open set $\Omega \subset \mathbb{R}^n$. The set Ω can be either the whole $\mathbb{R}^n$ or a bounded open set with uniformly C^2 boundary $\partial\Omega$. Let us denote by $\mathbf{n}(x)$ the outer unit vector normal to $\partial\Omega$ at x.

Let $\mathcal{A}$ be the differential operator

$$\mathcal{A}(x,D) := \sum_{i,j=1}^{n} a_{ij}(x)D_{ij} + \sum_{i=1}^{n} d_i(x)D_i + c(x)I, \tag{B.3}$$

where

$$D_i = \frac{\partial}{\partial x_i},\ D_{ij} = \frac{\partial^2}{\partial x_i \partial x_j},$$

I is the identity operator, and a_{ij}, d_i, c are real, bounded and continuous coefficients defined on $\overline{\Omega}$. We assume that for every $x \in \overline{\Omega}$ the matrix $a_{ij}(x)$, $i, j = 1, \ldots, n$ is symmetric and uniformly strictly positive definite, i.e., there exists a positive constant α such that

$$\sum_{i,j=1}^{N} a_{ij}(x)\xi_i\xi_j \ \geq \alpha|\xi|^2, \ x \in \overline{\Omega}, \ \xi \in \mathbb{R}^n. \tag{B.4}$$

Moreover, if $\Omega = \mathbb{R}^n$ we need the leading coefficients a_{ij} to be uniformly continuous.

We also consider a first order differential operator acting on the boundary:

$$\mathcal{B}u(x) := b_0(x)u(x) + \sum_{i=1}^{n} b_i(x)D_i u(x), \tag{B.5}$$

where the coefficients $b_i, \ i = 0, 1, \ldots, n$ are in $C^1(\overline{\Omega})$ and the following transversality condition holds:

$$\sum_{i=1}^{n} b_i(x)n_i(x) \neq 0, \ x \in \partial\Omega.$$

These hypotheses regarding operator $\mathcal{B}$ are needed in the following theorem

Theorem B.3.1. *Let $\Omega \subset \mathbb{R}^n$ be a bounded open set with uniformly C^2 boundary $\partial\Omega$, and $X = C(\overline{\Omega})$. We define the operator*

$$D(A) = \{u \in \bigcap_{1\leq p<+\infty} W^{2,p}(\Omega) : \mathcal{B}u_{|\partial\Omega} = 0, \ \mathcal{A}u \in C(\overline{\Omega})\},$$
$$Au = \mathcal{A}u, \ u \in D(A).$$

Then A is sectorial in X and $D(A)$ is dense in X.

B.4 Local existence results

Let us consider the initial-value problem

$$\frac{du}{dt} = Au(t) + F(t, \ u(t)) \ , \ t > 0, \tag{B.6}$$
$$u(0) = u_0, \tag{B.7}$$

where $A : \ D(A) \subset X \to X$ is a sectorial operator and $F : \ [0, \ T] \times X \to X$. We shall assume that F is continuous, and that for every $R > 0$ there is $L > 0$ such that

$$\|F(t,\ x) - F(t,\ y)\| \ \leq L\|x - y\|,\ t \in\ [0,\ T],\ \ x,\ y \in B(0,R),$$

where $B(0,R)$ denotes the open ball with center $0 \in X$ and radius R.
This means that F is Lipschitz continuous with respect to x on any bounded subset of X, with Lipschitz constant independent of t.

Definition B.4.1. *Let I be defined by $I = [0,\ \tau)$ or $I = [0,\ \tau]$, with $\tau \leq T$,*

- *We say that a function $u : I \to X$ is a strict solution of problem* (B.6)–(B.7) *in I if it is continuous with values in $D(A)$ and differentiable with values in X in the interval I, and it satisfies* (B.6)–(B.7).
- *We say that it is a classical solution if*
  - *it is continuous with values in $D(A)$ and differentiable with values in X in the interval $I\backslash\{0\}$,*
  - *it is continuous in I with values in X, and*
  - *it satisfies* (B.6)–(B.7).
- *We say that it is a mild solution if it is continuous with values in X, in $I\backslash\{0\}$, and it satisfies*

$$u(t) = e^{tA}u_0 + \int_0^t e^{(t-s)A}F(s,\ u(s))ds,\ t \in I. \tag{B.8}$$

One can prove that every strict or classical solution satisfies (B.8). Moreover, we notice that, in general, if u is a mild solution it may be discontinuous at $t = 0$ because, in general, $\lim_{t\to 0^+} e^{tA}u_0$, needs not to be u_0. However, one can prove that

$$\lim_{t\to 0^+} e^{tA}u_0 = \mathbf{u}_0\ \forall u_0 \in \overline{D(A)}.$$

Theorem B.4.1. *Let us denote by $C_b((0,\ a]; X)$ the Banach space of mappings from $(0,\ a]$ in X that are continuous and bounded. The following statements hold:*

a) If $u, v \in C_b((0,\ a]; X)$ are mild solutions for some $a \in (0,\ T]$, then $u \equiv v$.

b) For every $\bar{u} \in X$ there exist $r, \delta > 0, K > 0$ such that for $\|u_0 - \bar{u}\| \leq r$ problem (B.6)–(B.7) *has a mild solution $u = u(.; u_0) \in C_b((0,\ \delta]\ ; X)$. Function u belongs to $C([0,\ \delta]; X)$ if and only if $u_0 \in \overline{D(A)}$.*

Moreover for every $u_0, u_1 \in \mathcal{B}(u,\ r)$ we have

$$\|u(t; u_0) - u(t; u_1)\| \ \leq K\|u_0 - u_1\|,\ 0 \leq t \leq \delta.$$

B.5 The maximally defined solution

We can construct a maximally defined solution as follows.

Proposition B.5.1. *Set*

$$\tau(u_0) = \sup\{a > 0 : \text{ problem (B.6), (B.7) has a bounded mild solution } u_a \text{ in } [0,\ a]\}.$$

Then the mapping given by $u(t) := u_a(t)$, if $t \leq a$, *is well defined in the interval*

$$I(u_0) := \cup\{[0,\ a] : \text{problem (B.6), (B.7) has a mild solution } u_a \text{ in } [0,a]\}.$$

Besides, $\tau(u_0) = \sup I(u_0)$ *and* u *is the maximally defined solution corresponding to initial condition* u_0.

Now, we state some results concerning regularity of the maximally defined solutions.

Theorem B.5.1. *Assume that there is* $\alpha \in (0,1)$ *such that for every* $R > 0$ *we have*

$$\|F(t,\ x) - F(s,\ x)\| \leq C(R)(t-s)^{\alpha},\ 0 \leq s \leq t \leq T,\ \|x\| \leq R.$$

Then, for every $u_0 \in X, u \in C^{0,\alpha}([\varepsilon,\ \tau(u_0) - \varepsilon]; D(A)) \cap C^{1,\alpha}([\varepsilon,\ \tau(u_0) - \varepsilon]; X),\ \forall \varepsilon \in (0,\ \tau(u_0)/2)$. *Moreover the following statements hold:*

(i) If $u_0 \in \overline{D(A)}$ *then,* u *is a classical solution of* (B.6), (B.7).

(ii) If $u_0 \in D(A)$ *and* $Au_0 + F(0,\ u_0) \in \overline{D(A)}$, *then* u *is a strict solution of* (B.6)–(B.7).

In order to prove the next proposition, we introduce an auxiliary result.

Lemma B.5.1. *Let* $f \in C_b((0,\ T); X)$. *Then the function* v *defined by*

$$v(t) := \int_0^t e^{(t-s)A} f(s) ds,\ 0 \leq t \leq T,$$

belongs to $C^{\alpha}(0,\ T]; X)$ *for every* $\alpha \in (0,1)$, *and there is* $C = C(\alpha,\ T)$ *such that*

$$\|v\|_{\mathrm{C}^{0,\alpha}([0,T];X)} \leq C \sup_{0<s<T} \|f(s)\|.$$

Proposition B.5.2. *Let* u_0 *be such that* $I(u_0) \neq [0,T]$. *Then* $t \in I(u_0) \to u(t) \in X$ *is unbounded in* $I(u_0)$.

Proof. Assume by contradiction that u is bounded in $I(u_0)$ and set $\tau = \tau(u_0)$. Then $t \mapsto F(t,\ u(t;u_0))$ is bounded and continuous with values in X in the interval $(0,\ \tau)$. Since u satisfies the variation of constants formula (B.8), it may be continuously extended to $t = \tau$, in such a way that the extension is Hölder continuous in every interval $[\epsilon,\ \tau]$, with $0 < \epsilon < \tau$. Indeed, $t \mapsto e^{tA}u_0$ is well defined and analytic in the whole halfline $(0,\ +\infty)$, and $u - e^{tA}u_0$ belongs to $C^{0,\alpha}([0,\ \tau]; X)$ for each $\alpha \in (0,1)$ by Lemma B.5.1.

By Theorem B.4.1, the problem

$$\frac{dv}{dt}(t) = Av(t) + F(t,\ v(t))\ ,\ t \geq \tau,\ v(\tau) = u(\tau),$$

has a unique mild solution $v \in C([\tau,\ \tau+\delta]; X)$ for some $\delta > 0$. Note that v is continuous up to $t = \tau$ because $u(\tau) \in \overline{D(A)}$.

The function w defined by $w(t) = u(t)$ for $0 \leq t < \tau$, and $w(t) = v(t)$ for $\tau \leq t \leq \tau + \delta$, is a mild solution of (B.6)–(B.7) in $[0,\ \tau + \delta]$. This is in contradiction with the definition of τ. Therefore, u cannot be bounded. ■

From the above proof we can deduce the following result:

Corollary B.5.1. *If $I(u_0) \neq [0,T]$, then $\tau(u_0) = \sup I(u_0) \notin I(u_0)$.*

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Appendix C

Interpolation Error Estimates

This appendix includes some background on Lagrange finite element methods needed for the numerical analysis of the problem in Section 5.2: *Error estimates for the semidiscrete solution.* It has been mainly extracted from Ern and Guermond [27]. Other classical references on the mathematical analysis of the finite element method are Ciarlet [22] and Brenner and Scott [19]. We also include a discrete norm and some inverse-like inequalities following Wang's article [66].

The following definition of finite element has been given by Ciarlet [22].

Definition C.0.1. *A finite element consists of a triplet* $\{K,\ P,\ \Sigma\}$ *where:*

(i) K *is a compact, connected, Lipschitz subset of* $\mathbb{R}^d$ *with non-empty interior.*

(ii) P *is a vector space of functions* $p : K \to \mathbb{R}^m$ *for some positive integer* m*.*

(iii) Σ *is a set of* $n_{\rm sh}$ *linear forms* $\{\sigma_1,\ \ldots,\ \sigma_{n_{\rm sh}}\}$ *acting on the elements of* P*, such that the linear mapping*

$$P \ni p \to (\sigma_1(p),\ \ldots,\ \sigma_{n_{\rm sh}}(p)) \in \mathbb{R}^{n_{\rm sh}},$$

is bijective, i.e., Σ *is a basis for* $\mathcal{L}(P;\mathbb{R})$*. The linear forms* $\{\sigma_1,\ \ldots,\ \sigma_{n_{\rm sh}}\}$ *are called* ***local degrees of freedom****.*

C.1 Local interpolation operator

The first step is to define the local interpolation operator associated to a family of finite elements. It will be used in the next section to build the global interpolation operator that is the one we are interested in.

Let Ω be a domain in $\mathbb{R}^n$ and $\mathcal{T}_h = \{K_l\}_{1\leq l\leq n_{el}}$ be a mesh of Ω, where n_{el} is the number of elements in the mesh and $\overline{\Omega}_h = \bigcup_{k\in\mathcal{T}_h} K$ (Ω_h is called ***geometric interpolation of*** Ω). Let $\{\hat{K}, \hat{P}, \hat{\Sigma}\}$ be the reference finite element.

Denote by $\{\hat{\sigma}_1, ...\hat{\sigma}_{n_{dof}}\}$ the local degrees of freedom and by $\{\hat{\theta}_1, ...\hat{\theta}_{n_{dof}}\}$ the local shape functions. Let $V(\hat{K})$ be the domain of the local interpolation operator $\mathcal{I}_{\hat{K}}$ associated with $\{\hat{K}, \hat{P}, \hat{\Sigma}\}$, i.e.,

$$\mathcal{I}_{\hat{K}} : \hat{v} \in V(\hat{K}) \rightarrowtail \sum_{i=1}^{n_{dof}} \hat{\sigma}_i(\hat{v})\hat{\theta}_i \in \hat{P}.$$

For all $K \in \mathcal{T}_h$, one must first define the counterpart of $V(\hat{K})$, i.e., a Banach space $V(K)$ and a linear bijective mapping

$$\Phi_K : V(K) \to V(\hat{K}).$$

Then, a set of $\mathcal{T}_h$-based finite elements can be defined as follows:

Proposition C.1.1. *For $K \in \mathcal{T}_h$, the triplet $\{K, P_K, \Sigma_K\}$ defined by*

$$\begin{cases} K = T_K(\hat{K}) \\ P_K = \{\Phi_K^{-1}(\hat{p}) : \hat{p} \in \hat{P}\} \\ \Sigma_K = \{\{\sigma_{K,i}\}_{1\leq i\leq n_{dof}} : \sigma_{K,i}(p) = \hat{\sigma}_i(\Phi_K(p)), p \in P_K\} \end{cases} \tag{C.1}$$

*is a finite element. The local shape functions are $\theta_{K,i} = \Phi_K^{-1}(\hat{\theta}_i)$ $1 \leq i \leq n_{dof}$, and the associated **local interpolation operator** is*

$$\mathcal{I}_K : v \in V(K) \rightarrowtail \sum_{i=1}^{n_{dof}} \sigma_{K,i}(v)\theta_{K,i} \in P_K.$$

Remark C.1.1. *Let $\{\hat{K}, \hat{P}, \hat{\Sigma}\}$ be a Lagrange finite element. Then, one may choose $V(\hat{K}) = \mathcal{C}(\hat{K})$. Defining $V(K)$ in a similar way, the mapping*

$$\Phi_K : v \in V(K) \to \Phi_K(v) = v \circ T_K \in V(\hat{K})$$

is linear and bijective. Then, for all $K \in \mathcal{T}_h$, the finite element $\{K, P_K, \Sigma_K\}$ constructed in Proposition C.1.1 is a Lagrange finite element. Moreover, since

$$\sigma_{K,i}(v) = \hat{\sigma}_i(\Phi_K(v)) = \Phi_K(v)(\hat{a}_i) = v \circ T_K(\hat{a}_i),$$

setting $a_{K,i} = T_K(\hat{a}_i)$ for $1 \leq i \leq n_{dof}$, we infer that $\{a_{K,i}\}_{1\leq i\leq n_{dof}}$ are the nodes of $\{K, P_K, \Sigma_K\}$.

Now, we are in a position to define the global interpolation operator.

C.2 Global interpolation operator

Using the $\mathcal{T}_h$-based family of finite elements $\{K, P_K, \Sigma_K\}_{K\in\mathcal{T}_h}$ generated in Proposition C.1.1, a global interpolation operator $\mathcal{I}_h$ can be constructed as follows: firstly, choose its domain to be

$$D(\mathcal{I}_h) = \{v \in L^1(\Omega_h) : \forall K \in \mathcal{T}_h, v_{|K} \in V(K)\}.$$

For a function $v \in D(\mathcal{I}_h)$, the quantities $\sigma_{K,i}(v_{|K})$ are meaningful on all the mesh elements and for all $1 \leq i \leq n_{dof}\cdot$ Then, the global interpolant $\mathcal{I}_h v$ can be specified elementwise using the local interpolation operators defined above, i.e.,

$$\forall K \in \mathcal{T}_h, (\mathcal{I}_h v)_{|K} = \mathcal{I}_K(v_{|K}) = \sum_{i=1}^{n_{dof}} \sigma_{K,i}(v_{|K})\theta_{K,i}.$$

The global interpolation operator is defined as follows:

$$\mathcal{I}_h : v \in D(\mathcal{I}_h) \to \sum_{K\in\mathcal{T}_h}\sum_{i=1}^{n_{dof}} \sigma_{K,i}(v_{|K})\theta_{K,i} \in W_h,$$

where W_h, the codomain of $\mathcal{I}_h$, is

$$W_h = \{v_h \in L^1(\Omega_h) : \forall K \in \mathcal{T}_h, v_{|K} \in P_K\}.$$

The space W_h is called ***an approximation space***. Notice that, we abuse of notation by implicitly extending $\theta_{K,i}$ by zero outside K.

Definition C.2.1. *Let $\{a_1, \ldots, a_{n_{dof}}\}$ be the nodes associated to the finite element space and $\{\psi_{h,1}, \cdots, \psi_{h,n_{dof}}\}$ the global shape functions. The **global Lagrange interpolation operator** is defined as follows:*

$$\mathcal{I}_h : v \in \mathcal{C}(\overline{\Omega}_h) \to \sum_{i=1}^{n_{dof}} v(a_i)\psi_{h,i} \in V_h.$$

Notice that the domain of $\mathcal{I}_h$ can also be taken to be $H^s(\Omega_h)$ for $s > \dfrac{n}{2}$.

C.3 Some bounds for the interpolation operator

Let us start with a bound for the local intepolation operator which will be generalized later for the global one.

Lemma C.3.1. *Let $\{\hat{K}, \hat{P}, \hat{\Sigma}\}$ be a finite element with associated normed vector space $V(\hat{K})$. Let $1 \leq p \leq \infty$, and assume that there exists k an integer such that*

$$\mathbb{P}_k \subset \hat{P} \subset W^{k+1,p}(\Omega) \subset V(\hat{K}).$$

Let $T_K : \hat{K} \to K$ be an affine bijective mapping and $\mathcal{I}_K$ be the local interpolation operator on K. Let l be such that $0 \leq l \leq k$ and $W^{l+1,p}(\hat{K}) \subset V(\hat{K})$ with continuous embedding. Then, setting $\sigma_K = \dfrac{h_K}{\rho_k}$ (ρ_K is the diameter of the largest ball that can be inscribed in K and h_K is the diameter of K $h_K = \max_{x,y \in K} \|x - y\|$), there exists $c > 0$ such that, for all $m \in \{0, ..., l+1\}$,

$$\forall K \in \mathcal{T}_h, \forall v \in W^{l+1,p}(K) \quad |v - \mathcal{I}_K v|_{m,p,K} \leq c h^{l+1-m} \sigma_K^m |v|_{l+1,p,K}.$$

Remark C.3.1. *For a Lagrange finite element of degree k, $V(\hat{K}) = \mathcal{C}(\hat{K})$. Hence, the condition on l in the above lemma is $\dfrac{n}{p} - 1 < l \leq k$.*

Definition C.3.1. *A family of meshes is said to be **shape-regular** if there exists σ_0 such that $\forall h$, $\forall K$, $\sigma_K = \dfrac{h_K}{\rho_K} \leq \sigma_0$.*

*It is said **quasi-uniform** if and only if it is shape-regular and there exist a constant C such that, for all h and K, $h_K \geq Ch$.*

Lemma C.3.2. *Let p, k, and l satisfying the assumptions of Lemma C.3.1.*

Let Ω be a polyhedron and $\{\mathcal{T}_h\}_{h>0}$ be a shape-regular family of affine meshes of Ω. Denote by V_h the approximation space based on $\mathcal{T}_h$ and $\{\hat{K}, \hat{P}, \hat{\Sigma}\}$. Let $\mathcal{I}_h$ be the corresponding global interpolation operator. Then, there exists c such that, for all h,

- *for $p < \infty$, if $v \in W^{l+1,p}(\Omega)$,*

$$\|v - \mathcal{I}_h v\|_{L^p(\Omega)} + \sum_{m=1}^{l+1} h^m \left(\sum_{K \in \mathcal{T}_h} |v - \mathcal{I}_h v|_{m,p,K}^p \right)^{\frac{1}{p}} \leq c h^{l+1} |v|_{l+1,p,\Omega};$$

- *for $p = \infty$, if $v \in W^{l+1,\infty}(\Omega)$,*

$$\|v - \mathcal{I}_h v\|_{L^\infty(\Omega)} + \sum_{m=1}^{l+1} h^m \left(\max_{K \in \mathcal{T}_h} |v - \mathcal{I}_h v|_{m,\infty,K} \right) \leq c h^{l+1} |v|_{l+1,\infty,\Omega};$$

- *for $p = 2$ and $l > \frac{n}{2} - 1$, if $v \in H^{l+1}(\Omega)$,*

$$\|v - \mathcal{I}_h v\|_{L^\infty(\Omega)} + \sum_{m=1}^{l+1} h^m \left(\sum_{K \in \mathcal{T}_h} |v - \mathcal{I}_h v|_{m,2,K}^2 \right)^{\frac{1}{2}} \leq c h^{l+1-n/2} |v|_{l+1,2,\Omega}.$$

Remark C.3.2. *Consider a Lagrange finite element of degree k. Take $p = 2$ and assume $n \leq 3$. Then, from Remark C.3.1 one can take $1 \leq l \leq k$ and hence the previous inequality yields, for all $v \in H^{l+1}(\Omega)$,*

$$\|v - \mathcal{I}_h v\|_{\mathbf{L}^2(\Omega)} + h|v - \mathcal{I}_h v|_{1,\Omega} \leq ch^{l+1}|v|_{l+1,\Omega}.$$

This estimate is optimal if v is smooth enough, i.e., $v \in H^{k+1}(\Omega)$. However, if v is in $H^s(\Omega)$ and not in $H^{s+1}(\Omega)$ for some $s \geq 2$, increasing the degree of the finite element beyond $s - 1$ does not improve the interpolation error.

C.4 Some inverse inequalities

Lemma C.4.1 (**Global inverse inequalities**). *Let us assume the hypotheses of Lemma C.3.1. Let us also assume that the family of meshes $\{\mathcal{T}_h\}_{h>0}$ is quasi-uniform. Let l be such that $\hat{P} \subset W^{l,\infty}(\hat{K})$. Set $W_h = \{v_h : \forall K \in \mathcal{T}_h,\ v_h \circ T_K \in \hat{P}\}$. Then, using the usual convention if $p = \infty$ or $q = \infty$, there is c, independent of h, such that, for all $v_h \in W_h$ and $0 \leq m \leq l$,*

$$\left(\sum_{K\in\mathcal{T}_h} \|v_h\|^p_{l,p,K}\right)^{\frac{1}{p}} \leq ch^{m-l+\min(0,\frac{n}{p}-\frac{n}{q})}\left(\sum_{K\in\mathcal{T}_h} \|v_h\|^q_{m,q,K}\right)^{\frac{1}{q}}.$$

Remark C.4.1. *In the particular case $p = \infty$ and $q = 2$ the above inequality yields*

$$\|v_h\|_{L^\infty(\Omega)} \leq Ch^{-n/2}\|v_h\|_{L^2(\Omega)}\ \forall v_h \in W_h. \tag{C.2}$$

To estimate the interpolation of nonlinear terms in the error estimates we use Lemma 4.3 in [66] that we state below.

Let us introduce an auxiliary semi-norm in $\boldsymbol{\mathcal{C}}(\overline{\Omega})$ by

$$\|\boldsymbol{\chi}\|_h := \left(\sum_{l=1}^{N} |\boldsymbol{\chi}(x_i)|^2\right)^{1/2}.$$

Since $\hat{P}$ is finite-dimensional, we have the equivalence between norms on the reference element. Then, by using a straightforward homogeneity argument, the following lemma can be proved:

Lemma C.4.2. *There exist two strictly positive constants C_1 and C_2 independent of h such that*

$$C_1 h^{n/2}\|\chi_h\|_h \leq \|\chi_h\|_{L^2(\Omega)} \leq C_2 h^{n/2}\|\chi_h\|_h$$

for all $\chi_h \in V_h$.

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Appendix D

Resumen

En términos generales, un reactor químico puede entenderse como un recipiente utilizado para transformar ciertas especies químicas en los productos finales deseados. Estos recipientes pueden ser simplemente reactores ideales de tanque agitado en el caso más simple o reactores más complejos como pueden ser los reactores de lecho fijo. En cualquier caso, es importante que el tiempo de residencia dentro del reactor sea el suficiente como para que se produzcan las reacciones químicas esperadas.

En el ámbito de la ingeniería química, el diseño de los reactores abarca al menos tres campos: termodinámica, cinética y transferencia de calor. Así, si por ejemplo se produce una reacción en un reactor batch STR, una pregunta razonable sería cuál es la conversión máxima esperada. Esta es una cuestión de termodinámica. Si quisiéramos saber en cuánto tiempo debería transcurrir la reacción para lograr una conversión en los productos deseados, estaríamos haciéndonos una pregunta sobre la cinética (deberemos conocer no solo la estequiometría, sino también las tasas de la reacción). Finalmente, si queremos saber cuánto calor debe transferirse al reactor o desde él para mantener la condición isotérmica, estamos tratando un problema de transferencia de calor combinado con un problema termodinámico (deberemos saber si la reacción es endotérmica o exotérmica).

Después de la reacción química generalmente debe realizarse un tratamiento físico para purificar el producto y reciclar, si es necesario, el material que no ha reaccionado. La cantidad de material a producir es un factor clave para determinar qué tipo de reactor se debe usar. Para cantidades pequeñas suelen utilizarse en la industria normalmente reactores batch STR. Para grandes volúmenes, como en la industria petrolera, los reactores de flujo en pistón son comunes.

Para describir más detalladamente un reactor es necesario distinguir entre los diferentes tipos. Hay muchas clasificaciones en la literatura. Cada una de ellas realizada de acuerdo con alguna característica. Describiremos los esquemas más habituales de acuerdo con el artículo de Foutch [29]:

Tipo de operación: Esta clasificación se realiza de acuerdo con la configuración del reactor. Esta es la clasificación que usamos principalmente en la tesis (batch STR, semi-batch, CSTR, PFR o FBR son algunos de los diferentes nombres de reactor según su configuración).

1. *Batch STR*: los reactivos se introducen en el reactor solo en el momento inicial. No hay flujos de entrada ni de salida a lo largo del proceso.
2. *Semi-batch STR*: algunos de los reactivos se introducen en el reactor en el momento inicial; otros se introducen continuamente a lo largo del proceso.
3. *Reactor de tanque agitado (de flujo) continuo en estado transitorio (CSTR)*: los reactivos se introducen continuamente a lo largo del tiempo. También hay un flujo de salida a lo largo del proceso.
4. *Reactores de flujo en pistón*: es un reactor tubular donde se asume flujo en pistón. Es decir, la velocidad es constante en cualquier sección transversal del reactor.
5. *Reactores de lecho fijo*: el reactor de lecho fijo es un reactor cilíndrico con extremos convexos y un lecho relleno de partículas catalíticas de tamaño uniforme, que se inmovilizan o se fijan dentro del tubo.

Número de fases: Los reactores también se pueden clasificar por el número de fases presentes en el reactor en cualquier momento. Se denominan reactores *homogéneos* y *heterogéneos*. Los primeros representan los reactores con una sola fase (los STR son reactores homogéneos). El segundo contiene más de una fase. Varios tipos de reactores heterogéneos están disponibles debido a varias combinaciones de fases (como PFR o FBR).

Tipos de reacción: Esta clasificación se realiza teniendo en cuenta el tipo de reacciones que se están produciendo. Algunos de los más importantes son:

1. *Catalíticas:* reacciones que requieren la presencia de un catalizador para obtener por ejemplo las condiciones de velocidad necesarias para ese diseño de reactor en particular. Un ejemplo de este reactor es el FBR.

2. *No-catalíticas:* reacciones que no incluyen un catalizador homogéneo o heterogéneo. Son las opuestas a las anteriores.
3. *Autocatalíticas:* en estas reacciones, uno de los productos aumenta la velocidad de las reacciones.
4. *Biológicas:* reacciones que involucran células vivas (enzimas, bacterias, etc.).
5. *Polimerizaciones:* reacciones que involucran la formación de cadenas de polímeros moleculares.

Finalmente, dependiendo del destino final en la industria, consideramos una clasificación de acuerdo con dos motivaciones diferentes.

1. *Reactores industriales*: simulación de su funcionamiento con el objetivo final de optimizarlo económicamente modificando las condiciones de funcionamiento (condiciones iniciales, temperatura, ...).
2. *Reactores de laboratorio / planta piloto*: simulación (para la optimización del diseño del reactor: determinación de las condiciones geométricas y de operación óptimas para ese futuro reactor). El objetivo del diseño es determinar las características del reactor, como tuberías, válvulas o mezcladores. Por ejemplo, el reactor debe tener un volumen suficiente para permitir que la reacción alcance un nivel de conversión o permitir el intercambio de calor necesario.

El diseño del reactor requiere conocer, en primer lugar, el tipo de reacciones que tendán lugar en él y sus dimensiones y también el método de operación de acuerdo con el proceso químico deseado, como se explica en [24]. Pero en ese proceso es importante conocer también las reacciones químicas, en cualquiera de los reactores descritos, y las expresiones de velocidad de reacción (cinética) que deben a través de una expresión matemática. Para predecir el tamaño del reactor necesario para la obtención de la conversión deseada de reactantes a los productos finales, se requiere información sobre la composición y los cambios de temperatura, así como la velocidad de reacción, obtenidos de las ecuaciones de balance de moles y energía.

Suponiendo conocidos los datos disponibles de los experimentos y la estequiometría (las reacciones), debemos buscar una metodología de identificación. De hecho, hay varias técnicas disponibles en la literatura, como los métodos diferencial, integral e incremental [12]. El **método diferencial** compara el lado derecho del modelo con las derivadas de los datos. El **método incremental** trabaja con el concepto "extent", que nos proporciona una solución analítica de un nuevo sistema desacoplado. El **método integral** resuelve numéricamente el modelo y lo compara con los datos. En cualquier caso, se formula un problema de optimización, en función de los parámetros cinéticos. Además, para

la obtención de resultados más precisos es posible combinar algunos de estos métodos.

Previo al diseño del reactor, es importante estudiar estos modelos rigurosamente. El análisis matemático de los modelos mencionados ha despertado curiosidad desde hace muchos años hasta nuestros días. En particular, las ecuaciones generales de convección-difusión-reacción tienen un notorio interés científico. De hecho, se han estudiado desde diferentes enfoques y utilizando una variedad de métodos. Por ejemplo, bifurcaciones y estabilidad, teoría de semigrupos, perturbaciones singulares o siguiendo un enfoque variacional. Seguido de este análisis, naturalmente resulta necesario simular estos modelos. La resolución numérica de los mismos puede basarse en un esquema de diferencias finitas en la mayoría de los casos y en algunos otros en el método de elementos finitos.

Esta tesis se ha dividido en tres partes en las que pretende hacer un estudio exhaustivo de reactores resolviendo algunas cuestiones que hemos introducido ya, tanto teóricas como prácticas sobre ellos, además de dos apéndices en los que se describen herramientas y resultados útiles a lo largo del documento en aras de obtener un texto auto-contenido. A continuación, describiremos en detalle el contenido de cada una de las partes.

I Modelando reactores químicos

Una parte importante en el modelo es la velocidad de la reacción que a priori puede entenderse como un parámetro independientemente de la forma y la longitud del reactor. Sin embargo, induce variaciones en la temperatura y la composición y viceversa, estas magnitudes influyen en las velocidades de reacción. Por ello, el comienzo de capítulo 1 está dedicado a recordar algunos conceptos básicos sobre las especies y las reacciones químicas. También a las velocidades de reacción, recordando las más importantes a través de la literatura (como las que se describen en [46], [34] y [31]); y a la definición de la tasa de reacción según la ley de Arrhenius.

Ahora bien, dado que muchos procesos se han modelado tradicionalmente en la industria como reactores ideales: reactores de tanque agitado o de flujo en pistón, no podemos olvidarnos de ellos. De hecho, los primeros serán los protagonistas en la parte III. En los capítulos 1 y 2 derivamos el modelado matemático de reactores de tanque agitado (batch, semi-batch y CSTR) y reactores de flujo en pistón (PFR). Consideramos tanto el caso transitorio como el estacionario y asumimos que los reactores no tienen porqué ser adiabáticos ni isotérmicos, por lo que la temperatura y las concentraciones de las especies deben calcularse mediante los modelos

que se obtienen a partir de las ecuaciones de conservación de la masa y de la energía, respectivamente. Suponemos densidad constante.

En el capítulo 2, se describe el modelo general de convección-difusión-reacción que es el que después se reduce a dimensión 1 para presentar un caso particular, el PFR. El objetivo de describir este modelo en el Capítulo 2 es estudiar la existencia y unicidad de la solución, además de analizar el comportamiento del error en la solución. Todo esto para obtener finalmente la solución numérica del modelo.

En el capítulo 3 derivamos el modelo para reactores de lecho fijo, también llamados reactores de lecho empacado (PBR) o reactores catalíticos de lecho empacado. Nos centramos en los modelos continuos que se utilizan con frecuencia en algunos procesos industriales. Algunos de ellos son la oxidación del etileno y la oxidación del metanol al formaldehído. A pesar de la existencia de un tipo más nuevo de reactores, como los reactores de lecho fluidizado, los reactores de lecho fijo se utilizan ampliamente para el procesamiento a gran escala tanto en la industria del petróleo y como en la industria química básica.

De hecho, en la industria se suelen considerar un conjunto de tubos llenos de catalizador, generalmente dispuestos dentro de una gran carcasa del reactor. En este sentido, se supone que la temperatura en el tubo permanece constante y que las condiciones son iguales en cada tubo (hay un fluido alrededor del exterior de los tubos para mantener una temperatura adecuada). Aunque estas suposiciones no son ciertas en la práctica.

En nuestro caso, el término "reactor de lecho empacado" se relaciona con una única carcasa cilíndrica con cabezas convexas con un lecho fijo de partículas catalíticas de tamaño uniforme, que se inmovilizan o se fijan dentro del tubo. En ese tubo se introduce una mezcla fluida de reactivos en la entrada del reactor que se mueve a lo largo del reactor e interactúa con las partículas activas catalíticas. Las reacciones generalmente producen intercambios de calor. Así que, si es necesario, la temperatura se regula a través de la pared del tubo.

Consideramos los FBR como sistemas de reacción heterogéneos. Se supone un flujo en pistón, es decir, $\mathbf{v} = v\mathbf{e}_z$ donde z es la dirección axial.

El modelo para estos reactores se basa en las leyes de conservación para la masa, la energía y el momento y todas ellas nos conducen a un sistema de ecuaciones en derivadas parciales. Sin embargo, debido a la complejidad del sistema, la descripción de estos reactores debe simplificarse. Por esta razón, existen diferentes modelos de reactores de lecho empacado válidos. De hecho, cada problema debe analizarse para hacer las simplificaciones adecuadas. En algunos casos, el reactor puede considerarse como un modelo pseudo-homogéneo. Si las diferencias entre las fases fluidas y

sólidas son significativas, se deben considerar modelos heterogéneos como es nuestro caso. Además, tenemos en cuenta la resistencia intraparticular.

Consideramos el modelo multi-escala. El lecho se modela a nivel de micro-escala como un continuo de pequeñas partículas de material sólido que contienen el catalizador y que interactúan con el fluido (suponemos que estas partículas son esféricas, pero otras geometrías como el cilindro se pueden considerar mediante modificaciones directas en el modelo). El fluido se modela a nivel de macro-escala y a través de un medio poroso. Para el modelo de macro-escala, el efecto de la micro-escala se representa mediante términos fuente tanto en las ecuaciones de concentración de especies como en la ecuación de energía. A su vez, el modelo de micro-escala se acopla a las magnitudes de macro-escala a través de sus condiciones de contorno.

II Análisis matemático y solución numérica

El objetivo de esta parte es hacer un estudio exhaustivo del modelo sobre análisis matemático y solución numérica. Nos centramos en los reactores descritos en el Capítulo 2. Como ya hemos mencionado, las ecuaciones en los sistemas de reacción-difusión se han estudiado desde diferentes enfoques utilizando una variedad de métodos diferentes.

A través de esta parte, el objetivo es demostrar la existencia global de soluciones para sistemas de reacción de convección-difusión. La prueba de este teorema se basa en las técnicas de [55]. En este artículo, la existencia local de los sistemas de reacción-difusión se proporciona a través de la teoría de los semigrupos al considerar el problema parabólico semilineal. Nosotros utilizamos esta teoría para nuestro sistema parabólico de PDE de primer orden. Además nos serán necesarias ciertas hipótesis, como la condición de Hölder y la propiedad local de Lipschitz en el término de reacción. Esta teoría nos proporciona una solución continua única. Por supuesto, esta solución se entiende en el sentido débil. Volviendo a la solución global, las propiedades **(P)** y **(M)** que se verificarán debido a la forma de nuestro término de reacción particular (la ley de acción de masas) juegan un papel importante en la prueba de existencia. Las variables en nuestro problema representan la concentración de especies, por lo que la positividad de este es una propiedad natural. Construiremos una contracción y el teorema de punto fijo se aplicará para la solución local. En primer lugar, estudiaremos la existencia en L^2, pero el objetivo es el límite de L^∞.

Los problemas de control y optimización en ingeniería química y sus aplicaciones a menudo requieren muchas simulaciones numéricas de sistemas dinámicos a gran escala con diferentes condiciones. Si se desea una estrategia de control rápida o en tiempo real, una simulación numérica

directa de fuerza bruta no funciona bien. Es importante saber cómo se comporta el error. En el Capítulo 5 se obtiene una estimación de error siguiendo las técnicas en [63]. El enfoque propuesto se aproxima a la función no lineal por su interpolante de Lagrange. Para asegurarnos de que podemos hacer estas estimaciones, necesitamos probar previamente la existencia de la solución del problema semidiscreto que utilizamos en las estimaciones. Una vez realizado este estudio, es necesario obtener una solución numérica de los modelos que nos interesan desde el punto de vista práctico. Nos centramos en los modelos PFR y FBR. Para el primero usamos un esquema de diferencias finitas y el método de elementos finitos para el modelo FBR.

III Identificación en sistemas de reacción

Esta última parte está relacionada con la identificación del modelo. Más precisamente, en la identificación del mejor modelo cinético de una lista de formas funcionales propuestas y también en los valores de sus parámetros correspondientes en el proceso de optimización. Para resolver el problema, utilizamos una combinación de un método incremental y un método integral. Tales procesos de identificación generalmente se estudian en sistemas donde los fenómenos de interés se pueden observar de forma aislada, sin otros fenómenos físicos. Ese es el caso para la identificación de la cinética de una reacción en fase líquida, en la que en la mayoría de los casos se usa un reactor batch STR o un reactor semi-batch. Eso se explica en [17]. Por este motivo, nos centramos en los reactores de tanque agitado, utilizando un conjunto de datos experimentales y las reacciones que tienen lugar. También proporcionamos un catálogo de modelos cinéticos que contienen los parámetros a identificar. Describimos también la expresión general de esta cinética.

Como decíamos, utilizamos una combinación de un método incremental y un método integral, también conocido como método de identificación simultánea. El uso de estos dos métodos en cascada se puede replicar para algunos de los reactores más típicos como el reactor de tanque agitado (batch, semi-batch o CSTR) y el reactor de flujo en pistón; ambos ampliamente utilizados en la literatura y la industria. De hecho, una vez que las reacciones son fijas, podemos obligarlas a ocurrir en uno u otro reactor y esto será lo que hará que nuestra cinética identificada sea una u otra. Por supuesto, una herramienta importante para tener en cuenta es un conjunto de mediciones en el laboratorio que se incluirán en el ajuste de parámetros de estas cinéticas.

Hay que tener en cuenta que el primer método que describiremos se puede aplicar solo en los tipos de reactor STR y PFR; sin embargo, el segundo podría aplicarse incluso a nuestro modelo FBR.

El método incremental funciona con el concepto de "extent", que nos proporciona una solución analítica de un nuevo sistema desacoplado. En algunos casos, la solución dada por el método incremental es suficiente y podemos concluir el proceso de identificación, pero no siempre es así. Más en detalle, la idea de este método es descomponer la tarea de identificación en un conjunto de subproblemas, uno para cada modelo cinético. Por tanto, este método se caracteriza por el desacoplamiento de las ecuaciones de reacción mediante procedimientos algebraicos y la solución directa de las ecuaciones transformadas. Así, los modelos cinéticos y sus parámetros se pueden identificar en paralelo para todas las reacciones. Los parámetros se obtienen a través de una optimización local.

Nosotros presentamos una alternativa al método en el que la ecuación de balance de energía se trata de forma independiente. La ecuación de volumen del modelo se puede resolver al principio e independientemente. El resto de EDOs del sistema están acopladas. Por eso trabajamos en dos etapas: el sistema de concentraciones se reescribe como un sistema de extents desacoplado y la ecuación de temperatura se resuelve de manera independiente utlizando las medidas experimentales de las concentraciones.

Si es necesario mejorar la solución del método incremental, disponemos de una heurística basada en la búsqueda por entornos (VNS) [47]. Este método utiliza como valores iniciales de los parámetros aquellos previamente calculados por el método incremental. Se generan nuevas soluciones en el momento de la ejecución al hacer perturbaciones sucesivas tanto en la cinética como en los parámetros.

El valor del funcional coste del método integral se actualiza con la ayuda de las derivadas calculadas a través del método del adjunto cuando una nueva combinación de parámetros y modelos cinéticos mejoran la solución.

El método integral se basa en una comparación directa de las mediciones de concentraciones de especies calculadas a través del modelo teórico. A veces, también incluye la comparación entre temperaturas experimentales y teóricas. Debido a esto, este método es obviamente más costoso computacionalmente.

Las principales dificultades se encuentran en la gran cantidad de parámetros que aparecen en el funcional coste porque necesitamos identificar al mismo tiempo los parámetros de cada reacción; y en el cálculo de las derivadas con respecto a estos parámetros en el funcional coste.

Finalmente, necesitamos resolver numéricamente el modelo utilizando un esquema de diferencias finitas (BDF2 inicializado con un BDF1) en tiempo en cada evaluación del funcional coste. Simultáneamente, calculamos las derivadas del funcional utilizando el método del adjunto [6].

Apéndices

El Apéndice A resume las ecuaciones generales de la mecánica de medios continuos para mezclas de reactantes que pueden verse con mas detalle en el libro [8].

El Apéndice C se basa en los libros de Ciarlet [22] y de Ern y Guermond [27], donde se presentan el operador de interpolación de Lagrange global y algunas acotaciones para este operador; también se ha utilizado el artículo de Wang en [66] donde se incluye una equivalencia entre la norma en $\mathbf{L}^2$ y una norma euclídea. En los párrafos siguientes, enunciamos las desigualdades mencionadas que son necesarias para las estimaciones de error del problema semidiscreto en la Sección 5.2.

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